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EVALUATION OF A DIFFUSION/TRAPPING MODEL FOR HYDROGEN INGRESS IN HIGH-STRENGTH ALLOYS

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The ingress of hydrogen in various high-strength alloys was investigated with a view to characterizing their susceptibility to hydrogen embrittlement (HE). A potentiostatic pulse technique was applied to two precipitation-hardened iron-base alloys (AerMet 100 and alloy A-286), two Cu-containing alloys (Be-Cu and alloy K-500), and a superferritic stainless steel (UNS S44660) in 1 mol/L acetic acid-1 mol/L sodium acetate. The data were analyzed using a diffusion/trapping model to obtain the irreversible trapping constant (k) and hydrogen entry flux for each alloy. Irreversible trapping was negligible in overaged AerMet 100 but pronounced in the aged alloy. The order of the k values for AerMet 100 and two steels (4340 and 18Ni) previously studied inversely parallels their threshold stress intensities for stress corrosion cracking. Likewise, the k values of alloy A-286, 18Ni steel, and also alloy 718 from earlier work are consistent with test data for their relative resistance to HE. The results for AerMet 100 and alloy A-286 extend the previously reported correlation between k and HE resistance. Unaged Be-Cu is intrinsically more susceptible to HE than unaged alloy K-500. The type of heat treatment has a marked effect on the trapping behavior of alloy K-500. The intrinsic susceptibility of the annealed and aged alloy is twice that for the direct-aged alloy. The propensity of the S44660 alloy to undergo HE at cathodic protection potentials can be attributed to the absence of an oxide and hence the relatively unrestricted entry of H.

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PREFACE

This final report describes work performed under Office of Naval Research (ONR) Contract No. N00014-91-C-0263 in a continuation of our program to investigate hydrogen ingress into various high-strength alloys, particularly in terms of irreversible trapping, with a view to characterizing the susceptibility of the alloys to hydrogen embrittlement (HE). A technique called hydrogen ingress analysis by potentiostatic pulsing (HIAPP) was used to obtain anodic current transients for the alloys in 1 mol L^{-1} acetic acid/1 mol L^{-1} sodium acetate, and the transients were analyzed using a diffusion/trapping model under interface control conditions to evaluate the trapping constant and hydrogen entry flux in each case.

The report is presented as an Executive Summary followed by five sections that will eventually form papers for publication in journals or in conference proceedings:

1. "Hydrogen Trapping in Precipitation-Hardened Iron-Base Alloys."

2. "The Effect of Aging on Hydrogen Trapping in Copper-Containing Alloys."

3. "The Ingress of Hydrogen into a Superferritic Stainless Steel."

4. "The Resistance of High-Strength Alloys to Hydrogen Embrittlement," in *Proceedings of the Tri-Service Conference on Corrosion* (Wright-Patterson Air Force Base, Dayton, OH, 1994), in press.

5. "The Role of Traps in Determining the Resistance to Hydrogen Embrittlement," in *Proceedings of the 5th International Conference on Hydrogen Effects on Material Behavior*, N. R. Moody and A. W. Thompson, Eds. (The Minerals, Metals & Materials Society, Warrendale, PA, 1994), in press.

The first paper covers a high-strength steel (AerMet 100) and a stainless steel (A-286) and the next two concern Cu-containing alloys (Be-Cu and two heats of alloy K-500) and a superferritic stainless steel (Sea-Cure) in its standard, hydrogen-resistant, and intermediate grades. The final two papers review the progress made in characterizing hydrogen trapping in high-strength alloys studied during our program with ONR; some of the work reported there was supported by our earlier ONR contract, No. N00014-86-C-0233.

The principal investigator would like to acknowledge Mr. J. Eckenrod of Crucible Research for supplying samples of the three grades of Sea-Cure and Dr. M. Natishan, then at the David Taylor Research Center, Department of the Navy but now at the University of Maryland, for providing samples of the two heats of alloy K-500.

EXECUTIVE SUMMARY

High performance alloys are often required to possess a combination of properties such as strength, toughness, and corrosion resistance. However, their resistance to hydrogen embrittlement (HE) remains a concern in many situations. Microstructural defects in these and other alloys provide potential trapping sites for hydrogen and so can play a crucial role in determining an alloy's intrinsic susceptibility to HE. However, whether embrittlement will actually occur is also affected by the amount of hydrogen entering the alloy. Consequently, alloys need to be characterized in terms of both trapping capability and the rate of hydrogen entry to assess their likelihood of embrittlement.

This report describes work performed during a continuation of our program with the Office of Naval Research to investigate hydrogen ingress in various alloys, particularly in terms of irreversible trapping, with a view to characterizing the susceptibility of the alloys to HE. A technique referred to as hydrogen ingress analysis by potentiostatic pulsing (HIAPP) was used to obtain anodic current transients for the alloys in 1 mol L^{-1} acetic acid/1 mol L^{-1} sodium acetate containing 15 ppm As_2O_3. The transients were analyzed using a diffusion/trapping model under interface control conditions to evaluate the apparent trapping constant (k_a) and hydrogen entry flux in each case. Where possible, k_a was then used to determine the irreversible trapping constant (k) and the density of irreversible traps.

The first part of this work focused on investigating the trapping behavior of two precipitation-hardened iron-base alloys (AerMet 100 and alloy A-286). Overaged/annealed and aged specimens of AerMet 100 exhibited a marked difference in trapping. Irreversible trapping in the overaged specimen was negligible, which is consistent with its lack of particles such as carbides that are responsible for irreversible trapping in many high-strength alloys. The aged specimen, however, displayed a relatively high value of k, which is quite possibly associated with Mo_2C and Cr_2C particles precipitated during aging. The order of the k values for AerMet 100 and two high-strength steels (4340 and 18Ni) previously studied inversely parallels their threshold stress intensities for stress corrosion cracking (K_{ISCC}); that is, the lower the value of k, the higher the value of K_{ISCC}.

The value of k for alloy A-286 is lower than that for AerMet 100 and is intermediate between those for two Ni-base alloys (718 and 925) examined previously. Thus, alloy A-286 is intrinsically less susceptible than the three steels and alloy 718 but more so than alloy 925. The k values of the precipitation-hardened alloys, 718, A-286, and 18Ni steel, are consistent with test

data for their relative resistance to HE. The results for AerMet 100 and alloy A-286 appear to extend the previously reported correlation between k and HE resistance.

The second part of the study involved two Cu-containing alloys, Be-Cu and alloy K-500. The results were compared with those for a 77Cu-15Ni alloy (Marinel) and another heat of alloy K-500 studied in earlier work. The Be-Cu alloy (1.8-2.0Be) in the unaged condition has a higher k than that for unaged alloy K-500 (nominally 65Ni-30Cu) and therefore is intrinsically more susceptible to HE. The type of heat treatment was found to have a marked effect on the trapping behavior of alloy K-500. The value of k for alloy K-500 annealed and aged to a yield strength of 689-724 MPa is more than twice as large as that for a specimen cold-drawn and direct-aged to a yield strength of 1096 MPa. The value of k for the 77Cu-15Ni alloy aged to a yield strength of 793 MPa is similar to that of direct-aged alloy K-500.

The final part of the work addressed a superferritic stainless steel — Sea-Cure (UNS S44660) — in its standard grade, its hydrogen-resistant grade and an intermediate grade. The three grades proved difficult to investigate in terms of trapping. In all cases, hydrogen entry was still low when reduction of the surface oxide occurred at a charging potential of -0.6 V (SCE). As a result, negligible hydrogen entered the alloys, and so their trapping characteristics could not be determined. On the other hand, it was clear that the surface oxides were effective barriers to hydrogen entry and therefore that these superferritics should be resistant to HE in mildly acidic or near-neutral solutions, provided that the potential is less cathodic than -0.6 V (SCE). The propensity of superferritics to undergo HE in seawater when they are cathodically polarized to potentials in the range -0.9 to -1.4 V (SCE) can be attributed to the absence of an oxide and hence to the relatively unrestricted entry of hydrogen into the alloy. An effective way of rendering Sea-Cure more resistant to HE under these circumstances is to reduce the intrinsic susceptibility by controlling the number and type of carbide particles, as is apparently done for the hydrogen-resistant grade.

Section 1
HYDROGEN TRAPPING IN PRECIPITATION-HARDENED
IRON-BASE ALLOYS

ABSTRACT

The ingress of hydrogen into two precipitation-hardened alloys — AerMet 100 (Overaged and aged) and alloy A-286 (UNS K66286) — was studied using a technique referred to as hydrogen ingress analysis by potentiostatic pulsing (HIAPP). Values of the irreversible trapping constant (k) and the hydrogen entry flux were determined for these alloys in 1 mol L^{-1} acetic acid/1 mol L^{-1} sodium acetate. Overaged/annealed and aged specimens of AerMet 100 exhibited a marked difference in trapping. Irreversible trapping in the overaged specimen was negligible, which is consistent with its lack of particles such as carbides that are known to be responsible for irreversible trapping in many high-strength alloys. The aged specimen, however, displayed a relatively high value of k, which is quite possibly associated with Mo$_2$C and Cr$_2$C particles precipitated during aging. The order of the k values for AerMet 100 and two high-strength steels (4340 and 18Ni) previously studied inversely parallels their threshold stress intensities for stress corrosion cracking (K_{ISCC}); that is, the lower the value of k, the higher the value of K_{ISCC}. The value of k for alloy A-286 is lower than that for AerMet 100 and is intermediate between those for two Ni-base alloys (718 and 925) examined previously. Thus, alloy A-286 is intrinsically less susceptible than the three steels and alloy 718 but more so than alloy 925. The k values of the precipitation-hardened alloys, 718, A-286, and 18Ni steel, are consistent with test data for their relative resistance to HE. The results for AerMet 100 and alloy A-286 appear to extend the previously reported correlation between k and HE resistance.

INTRODUCTION

Various steels are used for aircraft components such as landing gear and arresting hooks, because of their high-strength characteristics. However, these steels must meet stringent requirements with respect not only to strength but also to fracture toughness and resistance to environmentally assisted cracking. One of the alloys that have been developed for aerospace applications is a martensitic steel —AerMet 100—that is strengthened by precipitation of Mo$_2$C and Cr$_2$C. This steel is reported to possess a balanced combination of the required properties, including a higher resistance to hydrogen-assisted cracking in 3.5% NaCl than 4340 steel and 18Ni

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steel.[1] However, precipitation-hardened martensitic iron-base alloys as a group tend to be rather prone to hydrogen embrittlement (HE).[2-4] Austenitic iron-base alloys such as A-286, in which the strength is imparted by precipitation of γ' phase composed of $Ni_3(Al,Ti)$, have also been found to undergo HE.[5-7] Thus, the possibility of HE remains a major concern in the use of high-strength iron-base alloys, irrespective of the type of matrix and strengthening precipitates.

The resistance of an alloy to HE is strongly affected by the interaction of hydrogen with microstructural defects that act as hydrogen traps.[8] The type of defect plays a crucial role in determining an alloy's intrinsic susceptibility to HE, with large irreversible (high binding energy) traps typically imparting a high susceptibility.[9,10] Hence, characterization of alloys in terms of irreversible trapping can allow their intrinsic HE susceptibility to be assessed and provide a basis for examining the effect of traps on the observed resistance to HE.

The entry and trapping of hydrogen in a wide range of high-strength alloys have been investigated in previous work using an electrochemical technique referred to as hydrogen ingress analysis by potentiostatic pulsing (HIAPP).[11-14] The rates of H entry and rate constants for irreversible trapping were determined, and it appeared that, for most of these alloys, there was a correlation between the intrinsic susceptibility, as represented by k, and the actual resistance to HE observed in mechanical tests.

In the present work, HIAPP was used to obtain the rates of H entry and irreversible trapping constants for AerMet 100 in the overaged and aged conditions and aged alloy A-286 (UNS S66286). AerMet 100 extends the range of high-strength steels (4340 and 18Ni) examined previously,[11,12] while alloy A-286 provides a comparison with two precipitation-hardened nickel-base superalloys (718 and 925) that had already been studied.[12] The research was aimed in part at characterizing the intrinsic susceptibility of each alloy to HE in terms of its irreversible trapping constant. The intrinsic susceptibilities for AerMet 100 and alloy A-286 were then compared with those for the previous two steels and Ni-base alloys, respectively, and with results for the actual resistance to HE observed in tests by other workers. A further goal was to determine the trap density where possible and thereby identify the principal irreversible trap in each alloy.

EXPERIMENTAL PROCEDURE

The composition of each alloy is given in Table 1-1. The AerMet 100 and alloy A-286 were supplied in the form of rods with a diameter of 1.36 cm and 1.27 cm, respectively. The AerMet 100 was received in an overaged/annealed (677°C/16 h) condition. It was subsequently solution treated at 885°C for 1 h, air cooled to 66°C over 1-2 h, then further cooled to -73°C for 1

h, and finally aged at 482°C for 5 h to give a yield strength of about 1834 MPa. As noted above, Mo_2C and Cr_2C are precipitated within the martensite during aging.

The alloy A-286 was used as-received in the solution-annealed (900°C/2h) and aged (720°C/16 h) condition. The yield strength of the aged alloy was 848 MPa. In addition to the γ' phase precipitated during aging, alloy A-286 also exhibited Ti-rich particles that appeared to becarbides. The characteristic dimension of the particles was determined to be 3 μm and the particle concentration was 6.6×10^{13} m^{-3}.

Details of the electrochemical cell and instrumentation have been given previously.[11] The test electrodes of each alloy consisted of a 1.27-cm length of rod press-fitted into a polytetrafluoroethylene sheath so that only the planar end surface was exposed to the electrolyte. The surface was polished before each experiment with SiC paper followed by 0.05-μm alumina powder. The electrolyte contained 1 mol L^{-1} acetic acid and 1 mol L^{-1} sodium acetate (pH 4.8) with 15 ppm As_2O_3 and was deaerated continuously with argon before and throughout data acquisition. The potentials were measured with respect to a saturated calomel electrode (SCE). All tests were performed at 22 ± 1°C.

The test electrode was cathodically charged with hydrogen at a constant potential E_c for a time t_c, after which the potential was stepped in the positive direction to a value 10 mV negative of the open-circuit potential E_{oc}. Anodic current transients were obtained over a range of charging times, typically from 5 to 60 s, at different overpotentials ($\eta = E_c - E_{oc}$). The open-circuit potential of the test electrode was measured immediately before each charging time and was also used to monitor the stability of the alloy surface.

RESULTS

The current transients were analyzed using a diffusion/trapping model based on a constant entry flux at the surface.[11,15] According to the model, the total anodic charge (C m^{-2}) is given by

$$q'(\infty) = FJt_c\{1 - e^{-R}/(\pi R)^{1/2} - [1 - 1/(2R)]\mathrm{erf}(R^{1/2})\} \qquad (1\text{-}1)$$

where F is the Faraday constant, J is the ingress flux in mol m^{-2} s^{-1}, and R = $k_a t_c$. The charge $q'(\infty)$ is equated to the charge (q_a) passed during the experimental anodic transients. The adsorbed charge is almost invariably negligible, so q_a can be associated entirely with absorbed H. k_a is an apparent trapping constant measured for irreversible traps in the presence of reversible traps. It is related to the irreversible trapping constant (k) by kD_a/D_L where D_a is the apparent diffusivity and D_L is the lattice diffusivity of H. The use of k as an index of the intrinsic susceptibility has been discussed elsewhere.[14]

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For aged AerMet 100 and alloy A-286, Eq. [1-1] could be fitted to the experimental data for q_a to obtain values of k_a and J, where J was independent of charging time at each potential. In the case of overaged AerMet 100, q_a increased linearly with t_c (Fig. 1-1), indicating that $k_a = 0$ and therefore that irreversible trapping was negligible. In contrast, the aged alloy exhibited moderately high values of k_a, which were indicative of pronounced irreversible trapping. Values of k_a and J for two tests with aged AerMet 100 are given in Table 1-2. In both tests, k_a was independent of charging potential, which is to be expected since the trapping characteristics should be unaffected by electrochemical conditions unless the traps become filled to a significant extent. The overall mean value of k_a was 0.069 ± 0.004 s^{-1}. The flux in general did not change significantly with overpotential.

Alloy A-286 also displayed irreversible trapping; data for k_a and J obtained from three tests are given in Table 1-3. In all three tests, k_a is independent of overpotential, the mean value of k_a for the three tests being 0.073 ± 0.005 s^{-1}. The flux, however, in contrast to that for aged AerMet 100, showed a marked increase with potential. The dependence of J on E_c was shown to be logarithmic (Fig. 1-2), which is characteristic of Nernstian-type behavior and implies that the surface coverage of adsorbed hydrogen responds rapidly to changes in potential.

DISCUSSION

Irreversible Trapping Constants

Evaluation of k from k_a requires that the effect of reversible trapping be taken into account. The minor alloying elements, either in their atomic form or as intermetallics that are precipitated during aging, are assumed to be largely responsible for reversible trapping in AerMet 100 and alloy A-286, though for different reasons. In the case of body-centered cubic (bcc) Fe, elements such as Cr are known to have a marked effect on the diffusivity.[16] For example, the addition of 5 at.% Cr to Fe decreases the diffusivity by two orders of magnitude at 27°C. Significant effects could therefore be expected with minor elements that act as reversible traps in alloys such as AerMet 100 with a martensite lattice. Moreover, based on the case of Cr, these effects are likely to dominate those from microstructural defects such as dislocations.

For face-centered cubic (fcc) alloys, defects such as vacancies or edge dislocations are unlikely to contribute significantly to reversible trapping, since the binding energy of hydrogen to defects such as vacancies or edge dislocations in an fcc lattice is somewhat (a factor of 4) smaller than the activation energy for diffusion.[17] Thus, reversible trapping in alloy A-286, which has an austenitic lattice, should be influenced more by composition than by microstructural defects.
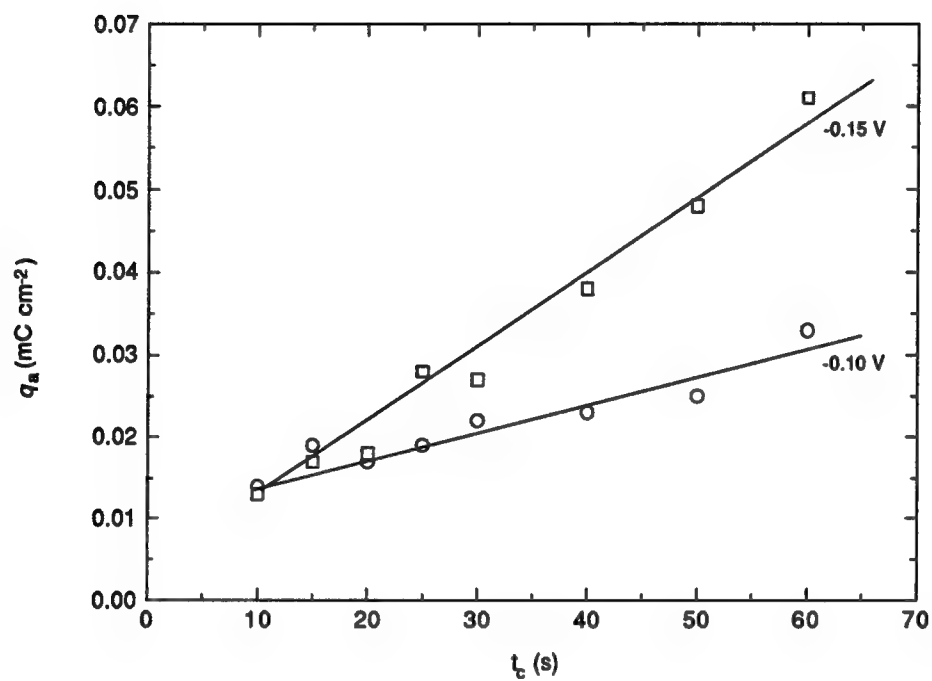
Figure 1-1. Dependence of anodic charge on charging time for
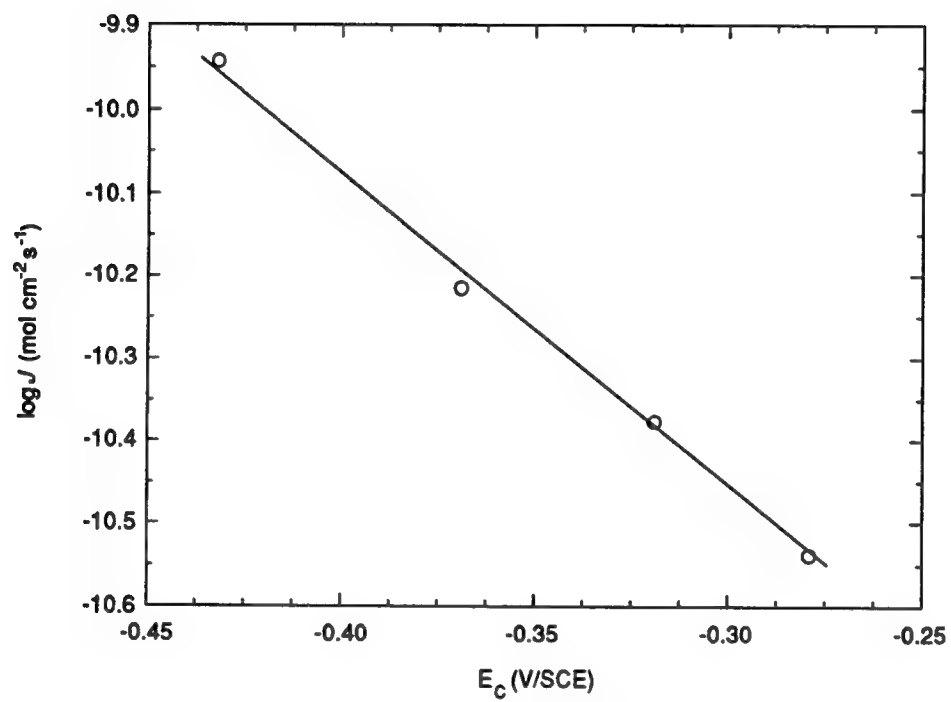overaged AerMet 100 at two charging potentials.

Figure 1-2. Dependence of entry flux on charging potential for alloy A-286.

The effect of reversible trapping is determined using the values of D_L and D_a, corresponding to the diffusivity for the "pure" alloy and for the actual alloy, respectively. Although Co is a prominent alloying element in AerMet 100, it is regarded as an anti-trap in Fe[8] and has been shown to have little effect on the diffusivity.[18] Thus, the pure alloys were assumed to be Fe-11Ni-3Cr for AerMet 100 and Fe-24Ni-14Cr for alloy A-286. Diffusivity data were not available for these alloys, so values were obtained for D_L by comparing data for annealed Fe-Cr and Fe-Ni alloys. It should be noted that, with the annealed alloys, the difference between D_a and D_L should reflect the contribution of dislocations as well as that of minor alloying elements to reversible trapping.

AerMet 100 contains 3% Cr, and, as noted above, Cr has a marked effect on the diffusivity, which can be attributed to its role as a trap.[8] The value of D_L for Fe-3Cr is $(5 \pm 1) \times 10^{-11}$ m^2 s^{-1} at 27°C.[16] It is uncertain whether Ni acts as a trap or an anti-trap.[8] Nevertheless, adding 11% Ni to Fe decreases the diffusivity by a factor of 23 ± 1, to $\sim 3 \times 10^{-10}$ m^2 s^{-1}, though this decrease may be associated more with the presence of an austenitic phase than with the composition directly.[19] Interestingly, the trapping energy (0.08 eV) for Ni, assuming it to be a trap, is believed to be slightly smaller than that for Cr (0.10 eV).[20] By assuming that the addition of 11% Ni causes a comparable decrease in the diffusivity for Fe-3Cr, whether by trapping or by affecting the type of lattice, D_L was estimated to be $(2.2 \pm 0.5) \times 10^{-12}$ m^2 s^{-1} for Fe-11Ni-3Cr.

Diffusivity data were not available for AerMet 100. However, the diffusivity for another precipitation-hardened steel — 18Ni maraging steel with a yield strength of 1723 MPa (250 ksi) — has been studied as a function of aging temperature[21] and was considered to provide the most appropriate value of D_a. 18Ni maraging steel has a nominal basic composition of Fe-18Ni-9Co and, after aging at 482°C, has a Rockwell C hardness (HRC) of 52, compared with a value of 55 for AerMet 100. The diffusivity for 18Ni (1723 MPa) maraging steel aged at 482°C is $(3.7 \pm 0.2) \times 10^{-13}$ m^2 s^{-1}. By using these values of D_a and D_L, k was calculated to be 0.41 ± 0.15 s^{-1}. In the case of overaged AerMet 100, k_a was roughly zero, which implies that $k = 0$.

For alloy A-286, the value of D_L for Fe-14Cr is $(1.2 \pm 0.2) \times 10^{-12}$ m^2 s^{-1}.[16] The addition of 24%Ni to Fe decreases the diffusivity[19] by a factor of 3500 ± 150 to $\sim 2 \times 10^{-12}$ m^2 s^{-1}. Such a large decrease is to be expected in view of the presence of a large volume fraction of austenite phase. Again, it was assumed that a comparable decrease would occur in Fe-24Ni-14Cr, and so the value of D_L for Fe-24Ni-14Cr was taken as $(3.4 \pm 0.7) \times 10^{-16}$ m^2 s^{-1}.

D_a for alloy A-286 was estimated from data for other austentic stainless steels. Diffusivities for alloys 301, 304, and 310 at 25°C were estimated by extrapolation from data[22] at temperatures from 100° to 350°C and are given in Table 1-4. H transport in austenitic stainless

steels is reported to be essentially independent of the austenite composition,[23] which is consistent with the values shown for these three alloys. The 24Ni and 14Cr in alloy A-286 are at the upper and lower ends of their respective ranges, so D_a was taken to have an intermediate value of $(3.5 \pm 0.5) \times 10^{-16}$ m^2 s^{-1}. The ratio of D_L to D_a is ~1, which might be expected for an alloy with such a low diffusivity; that is, reversible trapping should have a negligible effect when the activation energy for diffusion is large, as implied by the low values of D_a and D_L. Hence, for alloy A-286, k was approximately equal to k_a and so was taken as $0.073 \pm 0.0.031$ s^{-1}.

Comparison of Trapping Parameters

The trapping constants for AerMet 100 and alloy A-286 are compared with those for other steels and precipitation-hardened alloys, respectively, in Table 1-5. AerMet 100 has a lower k value than 4340 and 18 Ni maraging steel and therefore has the lowest intrinsic susceptibility to HE of the three steels. The order of the k values for these three steels inversely parallels their threshold stress intensities for stress corrosion cracking (K_{ISCC}) in 3.5% NaCl[1] (Fig. 1-3); that is, a lower value of k corresponds to a higher value of K_{ISCC}. The parallel between the trapping constant and K_{ISCC} supports the general view that hydrogen plays the dominant role in SCC of martensitic steels.[24] Thus, for these three steels, the observed resistance to HE, as represented by K_{ISCC}, appears to correlate with the intrinsic susceptibility, as represented by k. In other words, the observed resistance to HE appears to be determined primarily by the intrinsic susceptibility, with the entry flux having only a secondary effect.

Alloy A-286 is intermediate in its k value between alloys 718 and 925. Hence, it is intrinsically less susceptible than alloy 718 but more so than alloy 925. Measurements of the reduction in notch tensile strength and ductility in gas-phase charging tests have shown that alloy 718 undergoes extreme HE whereas alloy A-286 exhibits negligible embrittlement.[25] Corresponding measurements have also been made in cathodic charging tests on alloys 718 and A-286 aged to strengths that, relative to each other, were similar to those used in the present work. As in the gas-phase tests, it was found that alloy 718 undergoes a greater decrease in notch tensile strength and ductility than alloy A-286.[26] Thus, irrespective of the type of charging, the intrinsic susceptibility seems to parallel the relative resistance to HE for alloys 718 and A-286. The cathodic charging tests indicated that, the stronger the alloy, the greater the decrease in strength and ductility with increasing H concentration. However, in general, the observed resistance to HE is considered to be more directly an effect of microstructure than of strength.[24,27] In the case of alloys 718 and A-286, the trapping constants parallel the mechanical properties, so it is quite possible that the microstructure through its traps could be the key factor for these alloys too.
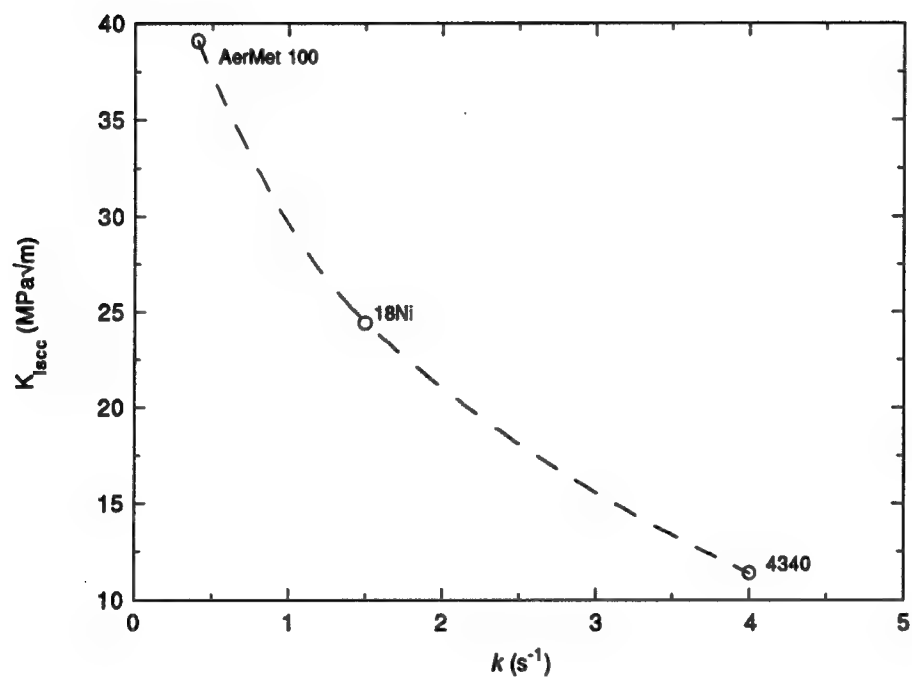
Figure 1-3. Variation of K_{ISCC} with k for high-strength steels.

The irreversible trapping constants for AerMet 100 and alloy A-286 are compared with the values for other alloys in Table 1-6. The value of k for alloy A-286 is lower than those for AerMet 100 and several Ni-base alloys, so alloy A-286 has a lower intrinsic susceptibility than the three steels and these Ni-base alloys. It has been found that alloy 718, like alloy A-286, is more resistant to HE than 18Ni (1723 MPa) maraging steel,[25] so the values of k for these three precipitation-hardened alloys are consistent with their relative resistances to HE observed in tests. The results for AerMet 100 and alloy A-286 therefore appear to extend the previously reported correlation between k and HE resistance to include these alloys.

A lack of appropriate mechanical test data in the literature makes it difficult to determine whether the position of alloy A-286 is justified with respect to that of alloy C-276 and the other precipitation-hardened alloy, 925; alloy 716 was found to be an exception to the correlation because its HE resistance appears to be determined by the H entry flux.[28] The difficulty in evaluating the relative position of A-286 is compounded by some uncertainty in the values of k, particularly for C-276. Nevertheless, on the basis of these values, it would be predicted that, in practice, the resistance of alloy A-286 to HE would be higher than that of alloy C-276 but less than that of alloy 925.

Identification of Irreversible Traps

The density of particles or defects (N_i) providing irreversible traps can be obtained from k_a according to Eq. [1-2][12,29]:

$$N_i = k_a a / (4\pi d^2 D_a) \qquad (1\text{-}2)$$

where a is the diameter of the metal atom and d is the trap radius. The value of a for an alloy is taken as the mean of the atomic diameters weighted in accordance with the atomic fraction of each element. The trap radius is estimated from the dimensions of heterogeneities that are potential irreversible traps, and trap densities are then calculated for the different values of d. In this way, the dominant irreversible trap can be identified by comparing the values of N_i with the actual concentrations of specific heterogeneities.

In the case of AerMet 100, aging causes precipitation of Mo_2C and Cr_2C within the martensite, as indicated above. Since irreversible trapping was negligible in the overaged/annealed alloy but pronounced in the aged alloy, it seems reasonable to assume that the carbides are the principal irreversible traps in the aged alloy. This assumption is consistent with our previous studies[11-14] showing that carbide and carbonitride precipitates are the predominant irreversible traps in many alloys.

For alloy A-286, the presence of the $Ni_3(Al,Ti)$ γ' phase precipitated during aging appears to be critical to the hydrogen-induced losses in ductility.[30] In particular, the misfit between γ' and the austenitic matrix is important with regard to planar slip and affects H accumulation at the particles.[31] Thus, γ' appears to provide irreversible traps in alloy A-286, though intermetallic precipitates in alloys such as maraging steels tend to be reversible traps.[12,32] Accordingly, the γ' precipitates are assumed to act as the principal irreversible traps in alloy A-286. For both alloys, however, the role of the Mo/Cr carbides and γ' as irreversible traps is speculative and has not been verified yet.

Although γ' has been implicated in the HE of alloy A-286, a value of N_i was calculated on the basis of the Ti-rich particles observed in this alloy, since Ti-carbide and carbonitride particles have often been identified as the principal irreversible traps in other alloys.[14] By using $D_a = (3.5 \pm 0.5) \times 10^{-16}$ m^2 s^{-1}, $d = 1.5 \times 10^{-6}$ m, and $a = 250 \times 10^{-12}$ m, N_i was found to be $(1.8 \pm 0.4) \times 10^{15}$ m^{-3}, whereas the actual concentration of Ti-rich particles was 6.6×10^{13} m^{-3}. The factor of 27 difference in the two values probably means that these particles are not the principal traps. This finding is consistent with the results of other work, in which it was found that the TiC phase could not be correlated with the overall hydrogen-induced ductility loss of alloy A-286.[31]

SUMMARY

- AerMet 100 exhibited a marked difference in trapping between overaged/annealed and aged specimens. The negligible irreversible trapping in the overaged specimen is consistent with its lack of particles such as carbides. The aged specimen, however, displayed a relatively high irreversible trapping constant, which is quite possibly associated with Mo_2C and Cr_2C particles precipitated during aging.

- AerMet 100 has a lower value of k than two other high-strength steels, 4340 and 18Ni maraging steel, and therefore has the lowest intrinsic susceptibility to HE of the three steels. For these steels, the observed resistance to HE, as represented by K_{ISCC}, appears to correlate with the intrinsic susceptibility, as represented by k.

- The value of k for alloy A-286 is lower than that for AerMet 100 and intermediate between those for the two Ni-base alloys, 718 and 925. Thus, alloy A-286 is intrinsically less susceptible than the three steels and alloy 718 but more so than alloy 925. The intrinsic susceptibilities (defined by k) of the three precipitation-hardened alloys (718, A-286, and 18Ni) are consistent with their observed resistances to HE. The results for AerMet 100 and alloy A-286 therefore appear to extend the previously reported correlation between k and HE resistance to include these alloys.

- The principal irreversible traps were assumed to be Mo_2C and Cr_2C in aged AerMet 100 and the $Ni_3(Al,Ti)$ γ' phase in alloy A-286. However, the role of both the carbides and γ' as irreversible traps has not been verified yet.

ACKNOWLEDGEMENTS

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Table 1-1
ALLOY COMPOSITION (wt%)

Element	AerMet 100	A-286
Al	0.005	0.13
B		0.0046
C	0.24	0.024
Co	13.47	0.08
Cr	3.00	14.02
Cu		0.10
Fe	71.00	57.08
Mg		-
Mn	0.01	0.28
Mo	1.19	1.37
N	<0.0010	
Nb+Ta		5.30
Ni	11.07	24.38
O	<0.0010	
P	0.002	0.019
S	<0.0005	0.001
Si	<0.01	0.22
Ti	0.009	2.09
V		0.20

Table 1-2
VALUES OF k_a AND J FOR AERMET 100

Test	η (V)	E_c (V/SCE)	k_a (s^{-1})	J (nmol cm^{-2} s^{-1})	Mean k_a
1	-0.10	-0.561	0.059	0.058	
	-0.15	-0.613	0.079	0.054	
	-0.20	-0.670	0.066	0.046	0.069 ± 0.006
	-0.25	-0.727	0.070	0.046	
2	-0.20	-0.666	0.068	0.059	0.069 ± 0.001
	-0.25	-0.722	0.069	0.061	

Table 1-3
VALUES OF k_a AND J FOR ALLOY A-286

Test	η (V)	E_c (V/SCE)	k_a (s^{-1})	J (nmol cm^{-2} s^{-1})	Mean k_a
1	-0.15	-0.279	0.075	0.029	
	-0.20	-0.319	0.070	0.042	0.077 ± 0.005
	-0.25	-0.369	0.075	0.061	
	-0.30	-0.432	0.086	0.114	
2	-0.15	-0.268	0.072	0.023	
	-0.20	-0.313	0.080	0.037	0.071 ± 0.006
	-0.30	-0.428	0.062	0.087	
3	-0.15	-0.258	0.074	0.026	
	-0.20	-0.296	0.064	0.041	0.071 ± 0.004
	-0.25	-0.346	0.074	0.059	

Table 1-4
DIFFUSIVITIES FOR AUSTENITIC STAINLESS STEELS

Alloy	Ni	Cr	D_a (m^2 s^{-1})
301	7	17	3.09×10^{-16}
304	9	18	3.49×10^{-16}
310	20	25	3.67×10^{-16}

Table 1-5
TRAPPING PARAMETERS

Alloy	Yield Strength (MPa)	k_a (s^{-1})	D_L/D_a	k (s^{-1})
Steels				
4340	1792	0.008 ± 0.001	500	4.0 ± 0.5
18Ni	1954	0.005 ± 0.002	300 ± 90	1.50 ± 1.05
AerMet 100	1834	0.069 ± 0.004	5.9 ± 1.8	0.41 ± 0.15
Precipitation-hardened alloys				
718	1238	0.031 ± 0.002	4.0 ± 0.5	0.124 ± 0.024
A-286	848	0.073 ± 0.005	1.0 ± 0.4	0.073 ± 0.031
925	758	0.006 ± 0.003	5.6 ± 0.6	0.034 ± 0.004

Table 1-6
IRREVERSIBLE TRAPPING CONSTANTS FOR RANGE OF ALLOYS

Alloy	Test Condition	k (s^{-1})
4340	HRC 53	4.0 ± 0.5
18Ni (300)	Aged	1.50 ± 1.05
AerMet 100	Overaged/annealed, aged	0.41 ± 0.15
716	Annealed, aged, 4% cold work	0.20 ± 0.06
718	Solution treated	0.124 ± 0.024
C-276	Hot rolled, 27% cold work	0.090 ± 0.030
A-286	Annealed, aged	0.073 ± 0.031
K-500	Cold drawn, aged	0.042 ± 0.006
Ti grade 2 (high H)	Annealed	0.040 ± 0.008
925	Annealed, aged	0.034 ± 0.004
Ti grade 2 (low H)	Annealed	0.028 ± 0.002
35N	Cold drawn, aged	0.026 ± 0.002
625	Annealed, 17% cold work	0.014 ± 0.010

Section 2
THE EFFECT OF AGING ON HYDROGEN TRAPPING
IN COPPER-CONTAINING ALLOYS

ABSTRACT

The irreversible trapping constants (k) and hydrogen entry fluxes were determined for two copper-containing alloys — alloy C17200 (Be-Cu) and alloy K-500 in two heats. A potentiostatic pulse technique was used to charge the alloys with hydrogen at various potentials in 1 mol L^{-1} acetic acid/1 mol L^{-1} sodium acetate. The results were compared with those for a commercial 77Cu-15Ni alloy and another heat of alloy K-500 studied in earlier work. The Be-Cu alloy (1.8 to 2.0Be) in the unaged condition has a higher k than that for unaged alloy K-500 (unannealed cold-drawn) and therefore is intrinsically more susceptible to HE. The type of heat treatment was found to have a marked effect on the trapping behavior of alloy K-500. The value of k for alloy K-500 annealed and aged to a yield strength of 689-724 MPa is more than twice as large as that for a specimen cold-drawn and direct-aged to a yield strength of 1096 MPa. The k value of 77Cu-15Ni alloy aged to a yield strength of 793 MPa is similar to that of direct-aged alloy K-500.

INTRODUCTION

Various copper-containing alloys can be precipitation-hardened to high yield strengths. Be-Cu alloys, for example, are strengthened by precipitation of (Cu,Co)Be in a matrix of α-Cu,[1] while in Ni-Cu alloys such as K-500, the strength is imparted by precipitation of γ' phase composed of $Ni_3(Al,Ti)$.[2] The capability of these alloys to be aged allows them to be used in a wide range of applications but does tend to make them more vulnerable to hydrogen embrittlement (HE), as observed for alloy K-500.[3]

HE in Ni-Cu base alloys is known to be assisted by S segregated at grain boundaries.[4] In Ni-base alloys, the presence of sulfide-formers such as Ti can often limit the grain boundary segregation of S,[5] but it is TiN particles that are usually present in alloy K-500.[6] The HE resistance of two Ni-base alloys —C-276 and 35N, which contained 0.8% Ti— was found to correlate with aging treatment, which in turn could be correlated with the concentration of grain boundary S and P.[7,8] The segregation of impurities in Cu-containing alloys may likewise be affected by aging and therefore affect the resistance to HE.

2-1

Microstructural defects in alloys provide potential trapping sites for hydrogen and so can play a crucial role in determining an alloy's resistance to hydrogen embrittlement (HE).[9] The local concentration of hydrogen trapped at a defect must reach some critical level (C_k) for cracks to be initiated.[9,10] Large irreversible (high binding energy) traps typically impart a high intrinsic susceptibility to an alloy because they have a relatively high probability of being located in a crack-sensitive region and therefore are associated with low values of C_k.[9] However, small irreversible traps may also be detrimental — that is, have a low C_k— if they lie in a vulnerable region such as a grain boundary. For example, in the case of alloy C-276, it has been suggested that an increased level of grain boundary P could reduce the critical concentration of H required for fracture.[7] Thus, the intrinsic susceptibility of an alloy to HE is highly dependent on the type of microstructural defect and could be increased considerably by segregation of impurities to grain boundaries.

The entry and trapping of hydrogen in a wide range of high-strength alloys have been investigated in previous work using an electrochemical technique referred to as hydrogen ingress analysis by potentiostatic pulsing (HIAPP).[11] The rates of H entry and rate constants for irreversible trapping were determined, and it was found that, for most of these alloys, there appears to be a correlation between the intrinsic susceptibility, as represented by k, and the actual resistance to HE observed in mechanical tests. These alloys included alloy K-500 (65Ni-30Cu) and Marinel[*] (77Cu-15Ni).[12] From an analysis of these alloys' trapping characteristics, it was concluded that the sulfur and phosphorus segregated at grain boundaries were probably the principal irreversible traps.

In the present work, the rates of H entry and trapping constants were obtained for three copper-containing alloys — alloy 17200 (Cu-2%Be) and two heats of alloy K-500 — by using HIAPP. The research was aimed at characterizing the intrinsic susceptibility of each alloy to HE in terms of its irreversible trapping constant. The hydrogen entry and trapping constants for these alloys were compared with those for the 77Cu-15Ni alloy and alloy K-500 studied previously, with the objective of relating these characteristics to the HE susceptibilities of the alloys.

EXPERIMENTAL PROCEDURE

The composition of each heat of alloy K-500 and, for comparison, the 77Cu-15Ni alloy is given in Table 2-1. The Be-Cu alloy contained 1.8/2.0 Be and was supplied as rod with a diameter of 6.35 mm. The alloy was received in an unaged condition with a Rockwell B hardness (HRB) of 93-95 (17-18 HRC), which corresponds to a yield strength of 585-613 MPa.

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[*] Trade name of Langley Alloys, Ltd. (Berkshire, England).

The two heats of alloy K-500 were supplied as sections of bar that had been solution-annealed and aged (AA) at 607°C for 16 h to give a yield strength in the range 689-724 MPa. The two heats are denoted as AA-1 and AA-2. Cylindrical specimens were machined from the sections of bar. In contrast to the present specimens, the alloy K-500 studied previously was supplied as cold-drawn (CD) rod that was direct-aged (DA) to give a yield strength of about 1096 MPa.

Details of the electrochemical cell and instrumentation have been given previously.[13] The test electrodes of each alloy consisted of a 3.8-cm length of rod (1.27 cm in diameter) press-fitted into a polytetrafluoroethylene sheath so that only the planar end surface was exposed to the electrolyte. The surface was polished before each experiment with SiC paper followed by 0.05-μm alumina powder. The electrolyte contained 1 mol L^{-1} acetic acid and 1 mol L^{-1} sodium acetate with 15 ppm As_2O_3 and was deaerated continuously with argon before and throughout data acquisition. The potentials were measured with respect to a saturated calomel electrode (SCE). All tests were performed at 22 ± 1°C.

The test electrode was cathodically charged with hydrogen at a constant potential E_c for a time t_c, after which the potential was stepped in the positive direction to a value 10 mV negative of the open-circuit potential E_{oc}. Anodic current transients were obtained over a range of charging times, typically from 5 to 60 s, at different overpotentials ($\eta = E_c - E_{oc}$). The open-circuit potential of the test electrode was measured immediately before each charging time and was also used to monitor the stability of the alloy surface.

RESULTS

The current transients were analyzed using a diffusion/trapping model that was based on a constant entry flux at the surface.[13,14] According to the model, the total anodic charge (C m^{-2}) is given by

$$q'(\infty) = FJt_c\{1 - e^{-R}/(\pi R)^{1/2} - [1 - 1/(2R)]\mathrm{erf}(R^{1/2})\} \qquad (2\text{-}1)$$

where F is the Faraday constant, J is the ingress flux in mol m^{-2} s^{-1}, and $R = k_a t_c$. The charge $q'(\infty)$ is equated to the charge (q_a) passed during the experimental anodic transients. q_a can be associated entirely with absorbed H, since the adsorbed charge is almost invariably negligible. k_a is an apparent trapping constant measured for irreversible traps in the presence of reversible traps. It is related to the irreversible trapping constant (k) by $k D_a/D_L$ where D_a is the apparent diffusivity and D_L is the lattice diffusivity of H.

For the constant flux model to be applicable, it must be possible to determine a trapping constant for which J is independent of charging time. Eq. [2-1] could in fact be fitted to the experimental data for q_a to obtain values of k_a and J that satisfy this requirement at each potential. Values of k_a and J for two tests on unaged Be-Cu are given in Table 2-2. In both cases, k_a is independent of charging potential, as is required for the model to be valid, since the trapping characteristics should be unaffected by electrochemical conditions at the metal surface. The overall mean value of k_a was 0.045 ± 0.006 s^{-1}. The flux was constant over the range of charging times for each overpotential and, as expected, increased with overpotential because of the dependence of J on the surface coverage of adsorbed hydrogen. The surface coverage is assumed to respond rapidly to changes in potential, so the flux should exhibit an exponential dependence on potential. Log J is indeed observed to vary linearly with η (Fig. 2-1), indicating that the coverage response is very fast.

The AA-2 specimen of alloy K-500 has not been tested yet and only a limited number of tests have been performed on the AA-1 specimen. Values of k_a and J for two tests on the AA-1 K-500 are given in Table 2-3. Based on the tests to date, k_a appears to be independent of charging potential and has a mean value of 0.060 ± 0.006 s^{-1}. In this case, the flux showed only a slight dependence on overpotential.

DISCUSSION

Irreversible Trapping Constants

The irreversible trapping constants (k) were derived from k_a by using diffusivity data for the "pure" alloy to obtain the lattice diffusivity (D_L) and for the actual alloy to obtain the apparent diffusivity (D_a), so that the effect of reversible traps could be taken into account. The "pure" alloy is considered to be Cu for Be-Cu and Cu-Ni for alloy K-500, so the minor alloying elements, either in their atomic form or as intermetallics that are precipitated during aging, are assumed to be largely responsible for reversible trapping in the actual alloys; for fcc alloys, defects such as vacancies or edge dislocations are unlikely to contribute significantly to reversible trapping, since the binding energy of hydrogen to defects such as vacancies or edge dislocations in an fcc lattice is somewhat (a factor of 4) smaller than the activation energy for diffusion.[15]

Be-Cu. The diffusivity of hydrogen in α-Cu over the temperature range 47°-657°C is given by[16]

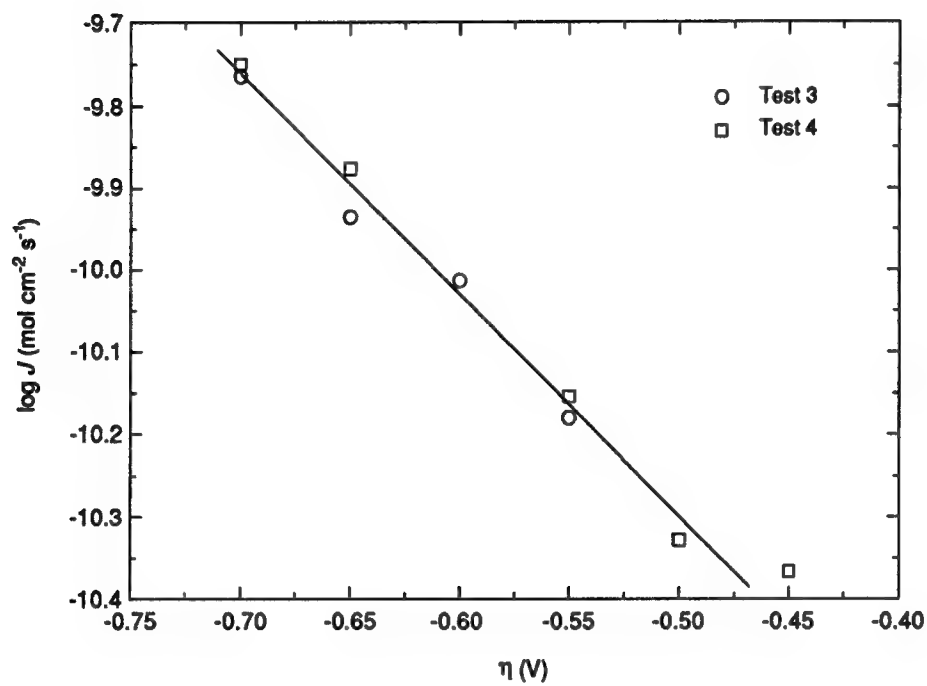$$D = 9.0 \times 10^{-7} \exp\left[-43.5 \text{ (kJ/mol)}/RT\right] \text{ m}^2 \text{ s}^{-1} \qquad (2\text{-}2)$$

Figure 2-1. Dependence of entry flux on overpotential for Be-Cu in two identical tests.

Extrapolation to 25°C gives a value of 2.1×10^{-14} m^2 s^{-1} at 25°C. The addition of 2% Be is unlikely to significantly affect the low diffusivity for copper. Hence, D_a for unaged Be-Cu is assumed to be similar in value to D_L, and so in this case, $k \sim k_a$.

No data were available for the diffusivity in the aged alloy. However, in the case of alloy K-500, the intermetallic particles appear to have little effect on D_a compared with that of the minor alloying elements in solid solution.[12] Hence, it was assumed that the intermetallic particles in Be-Cu also have little effect on D_a and k was taken to have the value of k_a.

Alloy K-500. The lattice diffusivity was determined by interpolation of data for a range of binary Cu-Ni alloys and was found to be $(3.0 \pm 0.1) \times 10^{-14}$ m^2 s^{-1} for 35 wt% Cu-65% Ni at 25°C.[16] The level of Cu differs a little between the 35Cu-65Ni alloy and alloy K-500 (30% Cu), but the error in using the diffusivity of the 35Cu alloy for D_L is considered to be negligible. The diffusivity for annealed and aged alloy K-500 (assumed to be at ambient temperature) is 1.90×10^{-14} m^2 s^{-1}, which is slightly higher than the value of 1.48×10^{-14} m^2 s^{-1} for the direct-aged alloy.[3] By using these data for D_L and D_a, k was found to be $0.0.096 \pm 0.013$ s^{-1} for AA-1 alloy K-500.

Comparison of Ingress Characteristics

The irreversible trapping constants for the range of Cu-containing alloys are listed in Table 2-4. They are also presented graphically in Fig. 2-2 to highlight differences between them. The Be-Cu alloy (1.8 to 2.0Be) in the unaged condition has a higher k than that for unaged alloy K-500 (unannealed CD) and therefore is intrinsically more susceptible to HE. The type of heat treatment has a marked effect on the trapping behavior of alloy K-500. The value of k for annealed and aged alloy K-500 (AA-1) with a yield strength of 689-724 MPa is more than twice as large as that for the direct-aged specimen with a yield strength of 1096 MPa. The k value for the aged 77Cu-15Ni alloy with a yield strength of 793 MPa is similar to that of direct-aged alloy K-500.

Mechanical tests have shown that the decrease in elongation was the same (71%) for direct-aged and annealed-aged alloy K-500 after cathodic charging for 16 h.[3] The loss in ductility can be defined in terms of the percent decrease in elongation, anal0gously to the reduction of area used by other workers,[17,18] and it is apparent that the observed resistance to HE is similar for the two types of aged alloy K-500 despite a difference in their intrinsic susceptibility. However, the entry flux was considerably higher (by up to a factor of 4) for the direct-aged specimen over the same range of overpotentials.[12] Thus, the similarity in HE resistance may result from the lower intrinsic susceptibility being largely balanced by a higher entry flux.
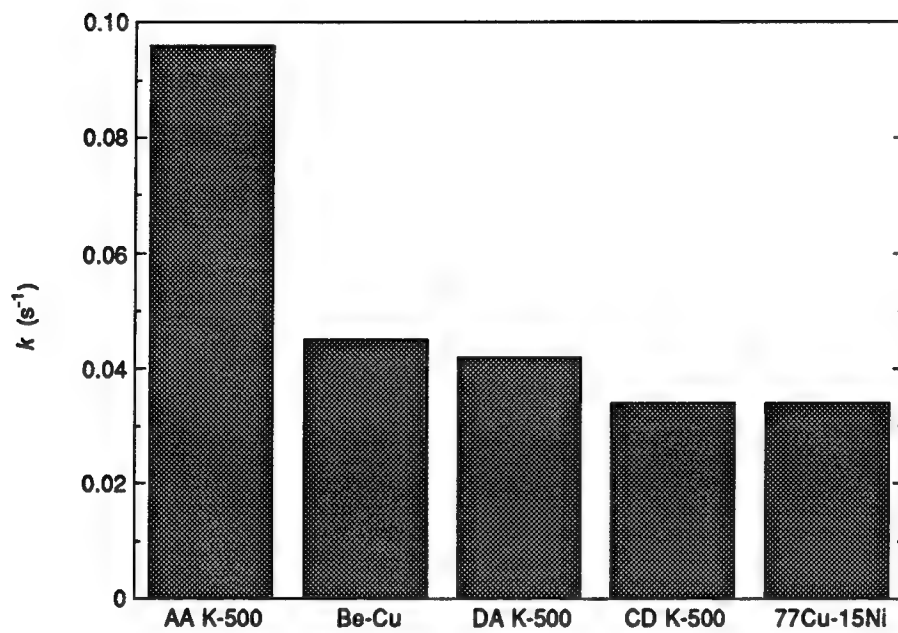
Figure 2-2. Variation in k for Be-Cu, the 77Cu-15Ni alloy, and alloy K-500 in annealed and aged (AA), direct-aged (DA), and cold-drawn (CD) unannealed/unaged conditions.

Identification of Irreversible Traps

The density of particles or defects (N_i) providing irreversible traps can be obtained from k_a, according to Eq. [2-3]:

$$N_i = k_a a / (4\pi d^2 D_a) \qquad (2\text{-}3)$$

where a is the diameter of the metal atom and d is the trap radius.[19,20] The value of a for an alloy is taken as the mean of the atomic diameters weighted in accordance with the atomic fraction of each element. The trap radius is estimated from the dimensions of heterogeneities that are potential irreversible traps, and trap densities are then calculated for the different values of d. In this way, the dominant irreversible trap can be identified by comparing the values of N_i with the actual concentrations of specific heterogeneities.

In the previous work on direct-aged alloy K-500, the irreversible traps predominantly encountered by hydrogen in alloy K-500 were assumed to be provided by sulfur segregated at grain boundaries.[12] This assumption was based on two factors: First, HE in Ni-Cu base alloys, as noted above, is assisted by sulfur segregated at grain boundaries[4] and hydrogen also probably segregates to the grain boundaries as in nickel.[21] Second, in the case of alloys C-276 and 35N, the calculated trap densities were in close agreement with the amount of grain boundary S and P distributed per unit volume (C_{gb}) of the alloy, whereas there were large differences between N_i and the bulk S-P content in these alloys.[11]

The absence of data for S segregation in alloy K-500 meant that the identity of the principal irreversible traps could not be verified by comparing N_i with the grain boundary concentration in this case. On the other hand, it was apparent that the principal traps were not associated with matrix S, since N_i was about 3 orders of magnitude less than the S content (1.6×10^{24} atoms m^{-3}) of the alloy. TiN particles present in alloy K-500 were likewise ruled out as the principal traps because of a large (2 orders of magnitude) difference between the corresponding value of N_i and the particle concentration. Further support was provided by results for the 77Cu-15Ni alloy, which was found to have a higher trap density than the 65Ni-30Cu alloy K-500.[12] Even allowing for some difference in the degree of segregation between the two alloys, the higher trap density was consistent with a higher level of grain boundary segregants, based on the higher S-P content (0.015 wt%) of the 77Cu-15Ni alloy.

A recent study, however, has suggested that intergranular cracking of AA alloy K-500 may be due to grain boundary carbon.[22] The two AA heats used in that study were the same as those in the present work. A bulk chemical analysis of AA specimens did not detect known embrittling elements such as P and S, nor did an energy dispersive spectroscopic analysis did not detect

embrittling elements on the fracture surfaces. However, high-resolution scanning Auger electron spectroscopy showed graphitic carbon to be located on the intergranular facets and within grain boundaries. The only significant compositional difference between the annealed-aged and direct-aged specimens is that their levels of Si are <0.05 and 0.15 wt%, respectively. However, there are clearly microstructural differences between them, as indicated by differences in hardness and yield strength.

SUMMARY

- Be-Cu (1.8 to 2.0Be) in the unaged condition has a higher k than that for unaged alloy K-500 (unannealed CD) and therefore is intrinsically more susceptible to HE.

- The type of heat treatment has a marked effect on the trapping behavior of alloy K-500. The value of k for the annealed and aged alloy (AA-1) is more than twice as large as that for a direct-aged specimen. However, the direct-aged alloy has a value of k similar to that of the aged 77Cu-15Ni alloy.

- The intrinsic susceptibility, as defined by k, of annealed-aged and direct-aged alloy K-500 differs markedly, yet other work has shown from the decrease in elongation that their HE resistance was similar. However, it is possible that the the difference in intrinsic susceptibility is compensated for by the considerable difference observed between the entry flux for these alloys.

- The primary irreversible traps in direct-aged alloy K-500 are believed to involve sulfur and phosphorus segregated at grain boundaries, but in the case of annealed and aged alloy K-500, there is evidence that graphitic carbon—not sulfur—is associated with HE.

ACKNOWLEDGEMENTS

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Table 2-1
COMPOSITION (wt%) OF Cu-CONTAINING ALLOYS

Element	K-500 DA	K-500 AA-1	K-500 AA-2	Marinel
Al	2.92	2.95	2.95	1.61
C	0.16	<0.17	<0.14	0.010
Cr				0.40
Cu	29.99	29.53	29.8	76.8
Fe	0.64	<0.85	<0.74	0.96
Mg				0.02
Mn	0.72	<0.70	<0.58	4.36
Nb				0.69
Ni	64.96	65.29	65.1	15.00
P			<0.002	0.010
Pb				0.007
S	0.001	<0.001	<0.001	0.005
Si	0.15	<0.05	<0.15	0.05
Sn				<0.02
Ti	0.46	0.46	0.44	
Zn				0.02

Table 2-2
VALUES OF k_a AND J FOR UNAGED Be-Cu

Test	η (V)	E_c (V/SCE)	k_a (s^{-1})	J (nmol cm^{-2} s^{-1})	Mean k_a
1	-0.55	-0.696	0.035	0.066	
	-0.60	-0.746	0.048	0.097	
	-0.65	-0.780	0.049	0.116	0.047 ± 0.006
	-0.70	-0.836	0.054	0.172	
2	-0.45	-0.620	0.045	0.043	
	-0.50	-0.659	0.038	0.047	
	-0.55	-0.694	0.035	0.070	0.044 ± 0.006
	-0.65	-0.778	0.051	0.133	
	-0.70	-0.841	0.052	0.178	

Table 2-3
VALUES OF k_a AND J FOR ALLOY K-500

Heat	Test	η (V)	E_c (V/SCE)	k_a (s^{-1})	J (nmol cm^{-2} s^{-1})	Mean k_a
AA-1	3	-0.25	-0.366	0.059	0.048	
		-0.30	-0.411	0.051	0.046	
		-0.35	-0.461	0.062	0.051	0.061 ± 0.006
		-0.40	-0.511	0.070	0.055	
	4	-0.25	-0.364	0.058	0.043	
		-0.30	-0.411	0.045	0.040	
		-0.35	-0.460	0.063	0.059	0.059 ± 0.006
		-0.40	-0.509	0.061	0.052	
		-0.45	-0.558	0.069	0.053	

Table 2-4
TRAPPING CONSTANTS FOR COPPER-CONTAINING ALLOYS

Alloy	State	Yield Strength (MPa)	k_a (s^{-1})	D_L/D_a	k (s^{-1})
K-500 (AA-1)	Annealed-aged	689-724	0.060 ± 0.006	1.6	0.096 ± 0.013
Be-Cu	Unaged	585-613	0.045 ± 0.006	~1	0.045 ± 0.006
K-500 (DA)	Direct-aged	1096	0.021 ± 0.003	2.0	0.042 ± 0.007
K-500 (CD)	Unaged	758	0.017 ± 0.003	2.0	0.034 ± 0.007
77Cu-15Ni	Aged	793	0.034 ± 0.004	~1	0.034 ± 0.015

Section 3

THE INGRESS OF HYDROGEN INTO A SUPERFERRITIC STAINLESS STEEL

ABSTRACT

The ingress of hydrogen into a superferritic stainless steel — UNS S44660, its hydrogen-resistant grade, and an intermediate grade — was studied using a technique referred to as hydrogen ingress analysis by potentiostatic pulsing (HIAPP). Anodic current transients were obtained for these alloys in 1 mol L^{-1} acetic acid/1 mol L^{-1} sodium acetate, but the three grades of UNS S44660 proved difficult to investigate in terms of trapping. In all cases, hydrogen entry was still low when reduction of the surface oxide occurred at a charging potential of -0.6 V (SCE). As a result, negligible hydrogen entered the alloys, and so their trapping characteristics could not be determined. On the other hand, it was clear that the surface oxides were effective barriers to hydrogen entry and therefore that these superferritics should be resistant to HE in mildly acidic or near-neutral solutions, provided that the potential is less cathodic than -0.6 V (SCE). The propensity of superferritics to undergo HE in seawater when they are cathodically polarized to potentials in the range -0.9 to -1.4 V (SCE) can be attributed to the absence of an oxide and hence to the relatively unrestricted entry of H into the alloy. An effective way of rendering the UNS S44660 alloy more resistant to HE is to reduce the intrinsic susceptibility by controlling the number and type of carbide particles, as has apparently been done for the hydrogen-resistant grade.

INTRODUCTION

Superferritic stainless steels such as Sea-Cure* (UNS S44660) and 29-4C (UNS S44735) are used for tubes in power plant condensers that are seawater-cooled. In many cases, the waterboxes and tube sheets in the condensers must be cathodically protected. However, the superferritics exhibit hydrogen embrittlement (HE) when they are polarized to potentials in the range -0.9 to -1.4 V (SCE).[1] This problem led to the development of a grade of the UNS S44660 alloy that is reportedly resistant to HE at cathodic potentials up to -2.0 V (SCE).[2] The new grade, which is designated as Sea-Cure Hy-Resist*, was obtained by restricting the combined C and N content to a maximum of 0.02% and replacing Ti by Nb. These compositional changes are presumed to affect the alloy's intrinsic susceptibility to HE by modifying the number and type of carbide particles, which are known to be strong hydrogen traps.[3] Thus, the differences observed

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* Trade names of Crucible Materials Corporation, Pittsburgh, PA.

in the HE resistance for the UNS S44660 alloy and its hydrogen-resistant grade should correspond to differences in their hydrogen trapping characteristics. In other words, the improvement in the HE resistance with the changes in stabilizing elements and impurity elements suggests that hydrogen trapping plays a crucial role in determining the resistance of these alloys to HE at highly cathodic potentials.

The entry and trapping of hydrogen in various alloys have been investigated in recent work using an electrochemical technique referred to as hydrogen ingress analysis by potentiostatic pulsing (HIAPP).[4] Values were determined for the rate of hydrogen entry and the rate constant for irreversible trapping (k). In addition, the trapping constants were analyzed to determine the density of particles or defects (N_i) providing irreversible traps. The objective of the present study was to determine the rate of H entry and trapping constants in the UNS S44660 alloy, its hydrogen-resistant grade and an intermediate grade. The research was aimed at characterizing the intrinsic susceptibility in each case to HE in terms of the irreversible trapping constant and then relating the intrinsic susceptibility to the observed resistance to HE.

EXPERIMENTAL PROCEDURE

The thickness and composition of each grade of the stainless steel are given in Table 3-1. The stabilizing element is Ti in the standard grade and Nb in the hydrogen-resistant grade, whereas the intermediate grade contains both elements. The other significant difference is that the hydrogen-resistant grade has much less C and N than either of the other grades. A minor change was also made in that small amounts of Cu and Al were added to the intermediate and hydrogen-resistant grades.

Details of the electrochemical cell and instrumentation have been given previously.[5] The three grades of Sea-Cure were supplied as sheet. Test electrodes were fabricated by machining a disk (1.27 cm in diameter) from each sheet and press-fitting it into a polytetrafluoroethylene sheath so that only one surface was exposed. The electrode surface was polished before each experiment with SiC paper followed by 0.05-μm alumina powder. The electrolyte contained 1 mol L^{-1} acetic acid and 1 mol L^{-1} sodium acetate with 15 ppm As$_2$O$_3$ and was deaerated continuously with argon before and throughout data acquisition. The potentials were measured with respect to a saturated calomel electrode (SCE). All tests were performed at 22 ± 1°C.

The test electrode was charged with hydrogen for times from 5 s to 60 s for each E_c. Anodic current transients with a charge q_a were obtained for each charging time over a range of cathodic overpotentials ($\eta = E_c - E_{oc}$). The open-circuit potential of the test electrode was sampled immediately before each pulse.

3-2

RESULTS

For most alloys, the charge (q_a) associated with the current transients can be analyzed using a diffusion/trapping model that has been derived for conditions imposed by the pulse technique.[6] The analysis yields values of the ingress flux (J) and an apparent trapping constant (k_a), which is used to determine the rate constant for irreversible trapping (k). However, all three grades of the UNS S44660 alloy showed little change in q_a with charging time at cathodic potentials up to reduction of the surface oxide at about -0.6 V (SCE).

It was evident that hydrogen entry does not increase enough with overpotential to become significant before the oxide is reduced. Thus, q_a must correspond almost entirely to oxidation of the adsorbed layer of hydrogen. If the adsorbed hydrogen is assumed to respond very rapidly to a change in potential, the surface coverage might be expected to exhibit an exponential dependence on overpotential. For all three alloys, log q_a was found to vary linearly with η (Fig. 3-1), which suggests that Nernstian-type conditions do in fact exist at the surface of the alloys with respect to the discharge reaction.

DISCUSSION

The amount of hydrogen that entered the UNS S44660 alloy and its other two grades during cathodic charging appears to have been negligible, as implied by the lack of change in q_a. As a result, the trapping constants could not be evaluated for any of the grades. On the other hand, the results did indicate that the surface oxides formed on these alloys in the acetate solution (pH 4.8) were effective barriers to hydrogen entry and therefore that these superferritics should be resistant to HE in mildly acidic or near-neutral solutions, provided that the potential was less cathodic than about -0.6 V (SCE). At more cathodic potentials when the oxide was reduced, hydrogen gas was evolved rapidly enough to produce bubbles on the alloy surface in the acetate solution.

The behavior of the UNS S44660 alloy is consistent with that observed for superferritics under cathodic protection in seawater. Although the pH of seawater is usually slightly alkaline (pH 8), the superferritics are unlikely to possess a surface oxide at highly cathodic potentials. Thus, the propensity of superferritics to undergo HE in seawater when they are cathodically polarized to potentials in the range -0.9 to -1.4 V (SCE) can be attributed to the absence of an oxide and hence to the relatively unrestricted entry of hydrogen into the alloy. Changes in the alloying elements that are designed to produce a modified surface oxide, and hence a modified rate of hydrogen entry, would clearly be irrelevant at highly cathodic potentials. Therefore, in the absence of coatings, the
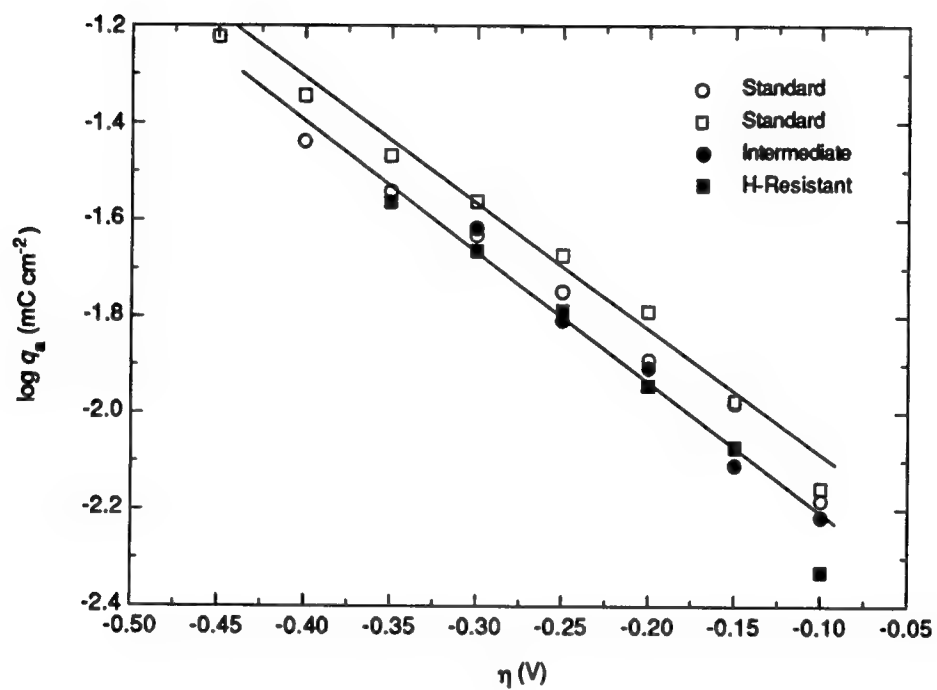
Figure 3-1. Dependence of log q_a on overpotential for the three grades of the UNS S44660 alloy. The two sets of data shown for the standard grade were obtained from identical tests.

most effective way of rendering the UNS S44660 alloy more resistant to HE is to reduce the intrinsic susceptibility by controlling the number and type of carbide particles, as has apparently been done for the hydrogen-resistant grade. It may be possible to determine the trapping constants of the three grades of the UNS S44660 alloy by coating the surface with palladium to enhance hydrogen entry at cathodic potentials where the oxide would be stable.

SUMMARY

- The surface oxides on the three grades of the UNS S44660 alloy were effective barriers to hydrogen entry. Hence, these alloys should be resistant to HE in mildly acidic or near-neutral solutions at potentials in the range of oxide stability.

- The propensity of superferritics to undergo HE in seawater when they are cathodically polarized to potentials in excess of -0.9 V (SCE) can be attributed to the relatively unrestricted entry of hydrogen into the alloy, as a result of the absence of a surface oxide.

- The resistance to HE of the UNS S44660 alloy is most effectively improved by reducing the intrinsic susceptibility in terms of carbide particles, since changes to the surface oxide and hence the rate of hydrogen entry would be of no consequence at highly cathodic potentials.

ACKNOWLEDGEMENTS

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Table 3-1
**COMPOSITION (wt%) AND THICKNESS OF THE UNS S44660
ALLOY AND MODIFIED GRADES**

Element	Standard	Intermediate	H-Resistant
Al		0.058	0.09
C	0.018	0.027	0.006
Cr	27.00	27.18	26.90
Cu		0.11	0.06
Fe	66.45	65.66	66.53
Mn	0.26	0.38	0.36
Mo	3.40	3.26	3.51
Nb+Ta		0.37	0.26
N	0.025	0.025	0.006
Ni	1.99	1.96	1.92
P	0.021	0.029	0.025
S	0.001	0.001	0.001
Si	0.40	0.66	0.33
Ti	0.44	0.28	
Thickness (mm)	2.3	2.1	2.6

Section 4
THE RESISTANCE OF HIGH-STRENGTH ALLOYS
TO HYDROGEN EMBRITTLEMENT*

ABSTRACT

The resistance of an alloy to hydrogen embrittlement (HE) is strongly influenced by the presence of microstructural heterogeneities, which can provide sites to trap hydrogen. The entry and trapping of hydrogen in a range of high-strength alloys have been investigated with a technique referred to as hydrogen ingress analysis by potentiostatic pulsing (HIAPP). Data were analyzed by using a diffusion/trapping model to determine entry and trapping parameters for high-strength steels, precipitation-hardened and work-hardened nickel-base alloys, and titanium alloys. For most of the alloys studied, the observed resistance to HE appeared to be determined primarily by the alloy's intrinsic susceptibility as defined by the trapping characteristics; that is, the H entry flux generally has only a secondary effect on the resistance to HE. However, in one case, the HE resistance was attributable to a low entry flux. This type of case highlights the need for characterizing alloys in terms of both trapping capability and rate of H entry to account for differences observed in their HE resistance.

INTRODUCTION

Microstructural heterogeneities in alloys provide potential trapping sites for hydrogen and so can play a crucial role in determining an alloy's resistance to hydrogen embrittlement (HE). This role originates in the fact that the interaction of these heterogeneities with hydrogen can strongly influence the series of events leading to failure.[1] The accumulation of hydrogen at second-phase particles and precipitates, for example, is generally considered to promote microvoid initiation via the fracture of particles or the weakening of particle-matrix interfaces. Traps with a large saturability and a high binding energy for hydrogen are highly conducive to HE,[2,3] whereas alloys containing a high density of well-distributed irreversible (high binding energy) traps that have a low saturability should be less susceptible. Thus, the intrinsic susceptibility of an alloy to HE is highly dependent on the type of microstructural defect, with large irreversible traps typically imparting a high susceptibility.

The basic concept of trap theory is that the local concentration of hydrogen trapped at a defect must reach some critical value (C_k) for cracks to be initiated.[1,3] It should be recognized, however, that the mechanism by which such an accumulation triggers HE is not addressed. The value of C_k, and therefore the intrinsic susceptibility of an alloy, is determined by the type of trap, its size, concentration (density), and other parameters. A decrease in C_k will render the alloy more susceptible. However, whether embrittlement will actually occur is also affected by the amount of trapped H, which depends on factors such as the entry kinetics, exposure time, and transport mode. In some cases, an alloy may prove resistant during exposure because the amount of H that enters is small enough that the critical concentration at the traps is not exceeded. Likewise, when alloys have a similar intrinsic susceptibility in terms of their trapping characteristics, the difference in their actual resistance to HE is likely to be determined by the amount of H absorbed by each alloy.

Over the last few years, the entry and trapping of hydrogen in a wide range of high-strength alloys have been investigated at SRI.[4-8] The rates of H entry and rate constants for irreversible trapping were determined using an electrochemical technique referred to as hydrogen ingress analysis by potentiostatic pulsing (HIAPP).[4,9] The research was aimed in part at characterizing the intrinsic susceptibility of the alloys to HE in terms of their irreversible trapping constants. The relative intrinsic susceptibilities then could be compared with results for the actual resistance to HE observed in tests by other workers. In this paper, the irreversible trapping constants and, where necessary, H entry fluxes for the different alloys are compared, with the objective of providing a basis for explaining differences in the resistance of these alloys to HE.

EXPERIMENTAL PROCEDURE

The alloy of interest is cathodically charged with hydrogen at a constant potential E_c for a time t_c, after which the potential is stepped in the positive direction. H diffuses back to the entry surface and is reoxidized, thereby generating an anodic current transient. Data are obtained over a range of charging times, typically from 5 to 60 s, at different overpotentials ($\eta = E_c - E_{oc}$) relative to the open-circuit potential (E_{oc}), which is measured immediately before each charging time. E_{oc} is also used to monitor the stability of the alloy surface, since any oxides present should not be reduced during charging.

The pulse technique was applied to high-strength steels,[4,5] precipitation-hardened and work-hardened nickel-base alloys,[5,6] and titanium.[7] The composition of each alloy is given in Table 4-1. Table 4-2 shows the yield strength of the alloys and the thermomechanical treatment used in each case.

Table 4-1
Alloy Composition (wt%)

	4340	18Ni	718	925	C-276	625	716	Ti Gr2
Al	0.031	0.13	0.60	0.30		0.18	0.22	
B		0.003	0.003					
C	0.42	0.009	0.03	0.02	0.002	0.03	0.011	0.021
Co		9.15	0.16		0.83		<0.01	
Cr	0.89	0.06	18.97	22.20	15.27	22.06	20.99	
Cu	0.19	0.11	0.04	1.93				
Fe	bal	bal	16.25	28.96	5.84	4.37	5.32	0.17
Mn	0.46	0.01	0.10	0.62	0.48	0.17	0.01	
Mo	0.21	4.82	3.04	2.74	16.04	8.70	8.10	
O	0.001							0.16
Nb+Ta			5.30			3.50	3.47	
Ni	1.74	18.42	54.41	40.95	57.5	60.33	60.5	
P	0.009	0.004	0.009		<0.005	0.012	0.004	
S	0.001	0.001	0.002	0.001	<0.002	0.001	0.001	
Si	0.28	0.04	0.11	0.17	<0.02	0.38	0.02	
Ti		0.65	0.98	2.11		0.27	1.35	bal
W		0.01			3.90			
Other	0.005N	0.05 Ca 0.02 Zr			0.12 V			<0.005H 0.007N

Test electrodes of each alloy were fabricated from a length (1.3-3.8 cm) of rod press-fitted into a Teflon sheath so that only the planar end surface was exposed to the electrolyte. The surface was polished before each experiment with SiC paper followed by 0.05-μm alumina powder.

Table 4-2
Thermomechanical Treatment of Alloys

Alloy	Heat Treatment[a]	Test Condition	Yield Strength (MPa)
4340	Annealed	HRC 41	1206
		HRC 53	1792
18Ni	Aged (482°C, 4 h)	As received	1954
K-500	Cold drawn, unaged	As received	758
		Aged (600°C, 8 h)	1096
35N	Cold drawn and aged	As received	1854
718	Hot fin., solution treated	As received	1238
925	Hot fin., annealed, aged	As received	758
C-276	Hot rolled	27% cold work	1237
625	Hot fin., annealed	17% cold work	1195
716	Annealed, aged	4% cold work	1186
Ti Gr2	Annealed (620°C, 1 h)	As received	380

[a] Provided by producer.

Details of the electrochemical cell and instrumentation have been given elsewhere.[4] The alloys were exposed in a deaerated solution containing 1 mol L^{-1} acetic acid and 1 mol L^{-1} sodium acetate with 15 ppm As$_2$O$_3$ added to promote H entry. The potentials were measured with respect to a saturated calomel electrode (SCE). All tests were performed at $22 \pm 2°C$.

ANALYSIS

Although permeation methods have been used extensively, they suffer from several disadvantages, as discussed elsewhere.[10] The main theoretical limitation is that most, if not all, diffusion/trapping models for these methods are based on an input boundary condition of constant concentration. Hence, these models are strictly applicable only for charging conditions without any entry limitation.

In the case of HIAPP, a model has been developed to allow for the effect of trapping on diffusion for cases involving either a constant concentration or a constant flux at the input surface.[4,9] The constant flux model was found to apply to all alloys studied to date. In this model, the rate of hydrogen ingress is controlled by diffusion but the entry flux of hydrogen is restricted, which results in interface-limited diffusion control. Solution of the diffusion equation for a constant flux condition gives the following expression for the total anodic charge (C m^{-2}):

$$q'(\infty) = FJ\,t_c\{1 - e^{-R}/(\pi R)^{1/2} - [1 - 1/(2R)]\mathrm{erf}(R^{1/2})\} \qquad (4\text{-}1)$$

where F is the Faraday constant, J is the ingress flux in mol m^{-2} s^{-1}, and $R = k_a t_c$. The charge $q'(\infty)$ is equated to the charge (q_a) associated with the experimental anodic transients. q_a can be associated entirely with absorbed H, since the adsorbed charge is almost invariably negligible.

k_a is an apparent trapping constant measured for irreversible traps in the presence of reversible traps. It is related to the irreversible trapping constant (k) by kD_a/D_L where D_a is the apparent diffusivity and D_L is the lattice diffusivity of H. The magnitude of k depends on the density of particles or defects (N_i) providing irreversible traps, the radius (d) of the trap defects, and the diameter (a) of the metal atom[11]:

$$k = \frac{4\pi d^2 N_i D_L}{a} \qquad (4\text{-}2)$$

The term $d^2 N_i$ represents the trapping capability and underlies the use of k as an index of an alloy's intrinsic susceptibility to HE.

For the constant flux model to be applicable, it must be possible to determine a trapping constant for which J is independent of charging time. Data for q_a could in fact be fitted to Eq. (4-1) to obtain values of k_a and J that satisfied this requirement at each potential. Experimental and fitted values of q_a for various charging times are compared in Fig. 4-1, which illustrates the level of agreement obtained for the alloys in this work.
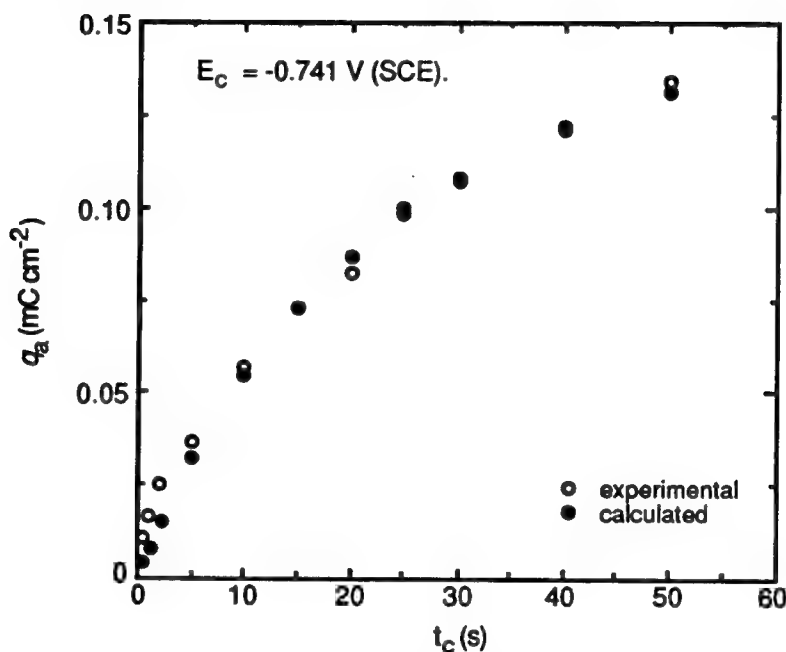

Figure 4-1. Dependence of anodic charge on charging time for Ti grade 2.

RESULTS

The alloys were studied as a series of groups, which were then merged to provide an overall comparison of the irreversible trapping constants. The values of k_a and k for each group are summarized in Table 4-3. The first group consisted of a high-strength steel (AISI 4340) and two nickel-containing alloys (K-500 and 35N).[4] The aim was to determine whether the irreversible trapping constants might assist in explaining differences observed in HE resistance between high-strength steels and nickel-base alloys. The values of both k and J for the steel were higher than those for alloys K-500 and 35N. Hence, both the irreversible trapping characteristics and the amount of H entering could account for the steel being less resistant to HE than the two nickel-containing alloys.

Two further groups of alloys were then studied: precipitation-hardened alloys (718, 925, and 18Ni maraging steel)[5] and work-hardened alloys (625 and C-276).[6] Alloys 625, 718, and

Table 4-3
Trapping Parameters

Alloy	k_a (s^{-1})	D_L/D_a	k (s^{-1})
4340 Steel	0.008 ± 0.001	500	4.0 ± 0.5
K-500 Unaged	0.017 ± 0.003	2.0	0.034 ± 0.006
Aged	0.021 ± 0.003	2.0	0.042 ± 0.006
35N	0.026 ± 0.002	1	0.026 ± 0.002
718	0.031 ± 0.002	4.0 ± 0.5	0.124 ± 0.024
925	0.006 ± 0.003	5.6 ± 0.6	0.034 ± 0.004
18Ni Steel	0.005 ± 0.002	300 ± 90	1.50 ± 1.05
	0.010 ± 0.005[a]	300 ± 90	3.00 ± 2.40
C-276	0.025 ± 0.003	3.6 ± 0.8	0.090 ± 0.030
	0.019 ± 0.010[a]	3.6 ± 0.8	0.068 ± 0.051
625	0.004 ± 0.002	3.6 ± 0.8	0.014 ± 0.010
716	0.054 ± 0.004	3.8 ± 0.8	0.20 ± 0.06
Ti grade 2	0.028 ± 0.002	1	0.028 ± 0.002
	0.012 ± 0.006[b]	1	0.012 ± 0.006

[a] Quasi-irreversible trapping. [b] Hydride formation.

925 were each characterized by a single type of irreversible trap, whereas alloy C-276 and 18Ni maraging steel were characterized by both an irreversible trap and a quasi-irreversible trap. In irreversible trapping, the rate constant for release is assumed to be zero, whereas for the quasi-irreversible case, the release constant is not zero but is too small to achieve local equilibrium between the lattice and trapped H.[5] The maraging steel had the highest value of k, followed by alloys 718, C-276, 925, and 625. It is apparent from its value of k that the maraging steel is intrinsically somewhat less susceptible than 4340 steel. Test results have in fact shown that 18 Ni(250) maraging steel is more resistant to cracking than 4340 steel,[12] so the differing susceptibility of the two steels was matched by their actual resistances to HE.

A similar parallel was found to exist for the 18Ni steel and alloy 718. Stress-rupture tests during electrolytic charging have shown that 18Ni (1723 MPa) maraging steel undergoes severe HE, whereas alloy 718 exhibits negligible embrittlement.[13] Likewise, gas-phase charging tests showed from the reduction in strength that the maraging steel was less resistant than alloy 718, although the embrittlement in both cases was characterized as extreme.[13]

No Ni-base alloys in the 900 series were included in the electrolytic embrittlement tests. However, gas-phase studies on alloy 903 have shown that short exposure to high-pressure hydrogen is not detrimental, though prolonged exposure, particularly at higher temperatures, can reduce ductility.[14] In contrast, alloy 718 undergoes extreme embrittlement under gas-phase charging, as noted above. These results suggest that alloy 903 and, by implication, alloy 925 are

4-6

less sensitive than alloy 718 to HE. Hence, the irreversible trapping constants of the three precipitation-hardened alloys are consistent with their relative resistances to HE observed in failure tests.

A similar comparison of the resistances of alloys C-276 and 625 is complicated by their sensitivity to cold work. However, the ranking of these alloys can be assessed indirectly from results for alloys C-276 and G.[15] Time-to-failure and crack propagation data showed that alloy C-276 has a greater tendency to HE than alloy G cold-worked to an equivalent degree. Alloys G and 625 are comparable in their levels of Cr, Mo, and Nb+Ta, so they might be expected to be similar in their resistance to HE. For the degree of cold work involved, alloy C-276 should therefore be less resistant to HE than alloy 625,[6] which coincides with the order of their trapping constants.

A lack of relevant data in the literature makes it difficult to determine whether the two cold-worked alloys fit in with the other alloys on the basis of their k values. The difficulty in evaluating the position of the cold-worked alloys is compounded by some uncertainty in these values. Nevertheless, the trapping constants for alloys 625 and 718 show a significant difference, and the sequence of values is consistent with results from C-ring and U-bend exposure tests that indicated alloy 625 is more resistant to cracking than alloy 718.[16]

If allowance is made for the uncertainty in k, the position of alloy 625 is comparable to that of alloy 35N. Tests using C-ring specimens of these alloys showed that the time-to-failure of unaged alloy 625 with 59% cold reduction is intermediate between those for 35% and 51% cold reduced alloy 35N in the aged condition.[17] Alloy 625 with 17% cold work, as was used in the present study, should withstand a longer exposure time than the same alloy with 59% cold work and therefore should be at least as resistant to HE as alloy 35N in the condition of interest (40-50% cold reduced and aged). In fact, the 625 specimen may be more resistant than the 35N alloy, as implied by their values of k. Thus, the order of the trapping constants parallels the relative resistance of these alloys to HE.

Ti grade 2 was also examined.[6] It exhibited two values of k, depending on the overpotential (Fig. 4-2) and therefore on the level of H in the alloy. Hydride precipitates have been observed in Ti grade 2 at H levels above ~100 ppm, but gross embrittlement does not result until much higher levels.[18] Thus, the similarity observed in the values of k for low-H Ti grade 2 and alloy 925 fits their relative resistance to HE in that both alloys must be exposed for long times to cause degradation of their mechanical properties.[14,18] Furthermore, the higher value of k for Ti grade 2 coincides with its decreased resistance to embrittlement at high enough H concentrations.

An exception to these trends was observed with alloy 716, which is an age-hardenable alternative to alloy 625.[16] Alloy 716 had a k of 0.2, which is the highest value among those for

the nickel-base alloys and indicates that this alloy is intrinsically the most susceptible to HE. However, tests with C-ring and U-bend specimens have shown that it is comparable to alloy 625 of similar yield strength in being able to withstand exposure in aggressive environments.[16] A likely explanation is that, although alloy 716 has a high intrinsic susceptibility, the H concentration at the dominant traps remains below the critical level required to initiate cracking. The entry flux was found to be low in the acetate buffer and could well have been low enough in the cracking test environments to delay failure in most cases (up to 1000 h). Thus, the resistance to cracking observed for alloy 716 was believed to be associated with the low entry flux of hydrogen.
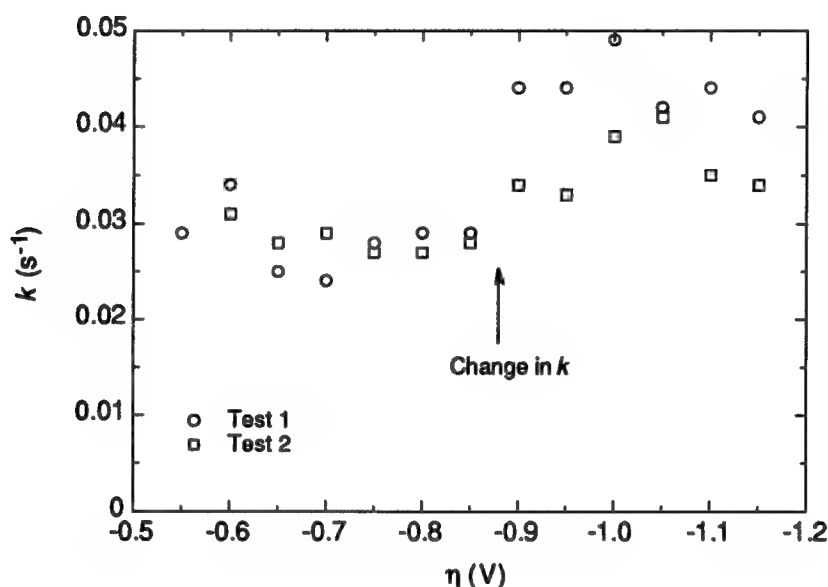

Figure 4-2. Variation in k with overpotential for Ti grade 2 in identical tests.

DISCUSSION

The alloys studied were generally characterized by a single type of irreversible trap, but in some alloys the principal irreversible type of trap was supplemented by other traps of either a quasi-irreversible type or another irreversible type. Values of k associated with the principal irreversible traps are listed in Table 4-4 for all the alloys except 716. They are also presented graphically in Fig. 4-3 to highlight differences between them.

The steels, particularly 4340, exhibit high values of k that are indicative of a high intrinsic susceptibility to HE, whereas the nickel-base alloys are characterized by lower values of k and are therefore intrinsically less susceptible. Differences in the susceptibility of the nickel-base alloys are smaller than those for the steels but are clearly discernible. In particular, the trapping constants for

alloys within groups defined by thermomechanical treatment (precipitation- and work-hardening) indicate that the susceptibilities can vary significantly.

Table 4-4
Irreversible Trapping Constants

Alloy	k (s^{-1})
4340 steel	4.0 ± 0.5
18Ni (300) steel	1.50 ± 1.05
718	0.124 ± 0.024
C-276 (27% cold work)	0.090 ± 0.030
K-500	0.042 ± 0.006
Ti grade 2 (high H)	0.040 ± 0.008
925	0.034 ± 0.004
Ti grade 2 (low H)	0.028 ± 0.002
35N	0.026 ± 0.002
625 (17% cold work)	0.014 ± 0.010

For most alloys, there appears to be a correlation between the intrinsic susceptibility, as represented by k, and the actual resistance to HE observed in failure tests. This correlation suggests that the observed resistance to HE is determined primarily by the alloy's intrinsic susceptibility — that is, by the irreversible trapping characteristics. Thus, the entry flux generally has only a secondary effect on the HE resistance.

Exceptions to this correlation can be expected in cases where the ingress flux for an alloy is low enough that the alloy is relatively resistant to cracking even though it might have a high
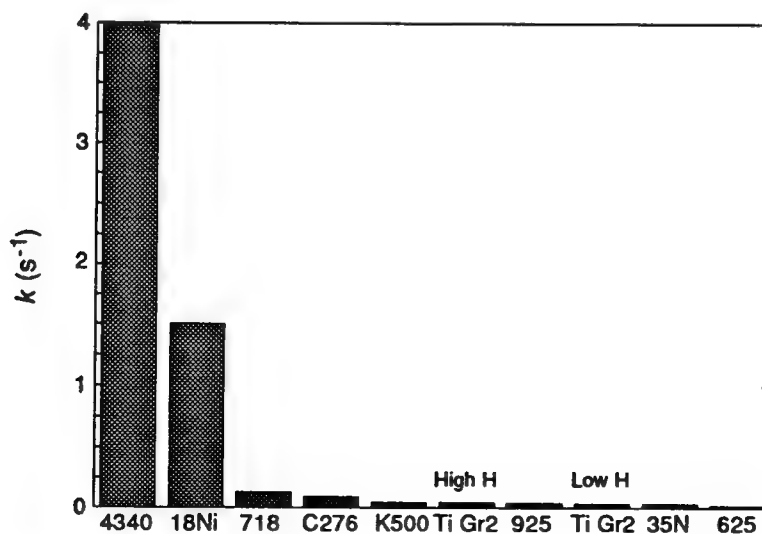

Figure 4-3. Variation in k for the different alloys.

intrinsic susceptibility. Such an exception was observed with alloy 716. The intrinsic susceptibility of this alloy was shown to be high ($k = 0.2$), yet the entry flux was apparently low enough that the alloy generally did not undergo cracking during exposure in aggressive environments for periods up to 1000 h.

The use of k to provide an index of HE susceptibility can be justified on the basis of Eq. (4-2), but there remains the question of why such a relatively simple parameter has the apparent ability in most cases to indicate the relative resistance actually observed to HE. Some insight may be gained by considering k, which encompasses the trapping capability (d^2N_i) as well as the alloy-specific characteristics of metal atom size and lattice diffusivity. The trapping capability has a strong influence on the critical concentration (C_k) required to initiate cracking at traps, while the diffusivity reflects the ease of H transport to different sites, including traps. Since the likelihood of crack initiation is highly dependent on both C_k and H accumulation, it is perhaps not surprising that k is effective as an index of susceptibility in being able to indicate the actual resistance of most alloys to HE. Underlying this rationale is the implication that, despite differences between alloys, the H entry flux is generally not low enough to become the controlling factor.

Finally, it should be noted that the density of particles or defects providing irreversible traps can be calculated from k, or k_a, by using Eq. (4-2). The trap radius (d) is estimated from the dimensions of heterogeneities that are potential irreversible traps, and trap densities are then calculated for the different values of d. In this way, the dominant irreversible trap can be identified by comparing the values of N_i with the actual concentrations of specific heterogeneities. Identification of the primary irreversible traps in the various alloys is described elsewhere.[4-8]

SUMMARY

For a wide range of alloys, a correlation exists between the intrinsic susceptibility, as defined by the irreversible trapping constant, and the observed resistance to HE. Thus, the HE resistance appears to be determined primarily by the alloy's intrinsic susceptibility. This relationship implies that generally the H entry flux has only a secondary effect on the HE resistance, suggesting that it is not low enough to become the controlling factor for most alloys. However, in one case (alloy 716), the resistance to HE can be attributed to a low entry flux.

The irreversible trapping constant, by virtue of the observed correlation, appears to be an indicator of the relative resistance to HE for most alloys, and as such, it can be used to predict the relative resistance of alloys in a particular environment. However, the predicted relative resistance may not be reliable in cases where H entry is severely restricted. The ability of k to provide an indication of the relative resistance to HE seems to be attributable to its dependence on both the

trapping capability and the diffusivity. The combination of these two characteristics is crucial for crack initiation and therefore provides a rationale for the correlation observed between k and the actual resistance to HE.

ACKNOWLEDGMENT

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Section 5

THE ROLE OF TRAPS IN DETERMINING
THE RESISTANCE TO HYDROGEN EMBRITTLEMENT*

Abstract

The ability of microstructural heterogeneities to act as hydrogen traps can critically affect the resistance of an alloy to hydrogen embrittlement (HE), so a knowledge of the alloy's trapping characteristics is crucial in accounting for the role of these heterogeneities. The entry and trapping of hydrogen in a range of high-strength alloys have been investigated using a technique referred to as hydrogen ingress analysis by potentiostatic pulsing (HIAPP) to determine the entry flux and the rate constant (k) for irreversible trapping. For most of the alloys, the observed resistance to HE appears to be determined primarily by the alloy's intrinsic susceptibility defined by k; that is, the entry flux generally has only a secondary effect on the resistance to HE. Analysis of the trapping constants allowed identification of various microstructural heterogeneities as the principal irreversible traps, either singly or in combination. The size and density of the irreversible traps were primary factors underlying the intrinsic susceptibility to HE. For example, alloys such as 718 and 4340 steel that contained large particles as the primary irreversible traps were found to have high intrinsic susceptibilities (high values of k). Thus, it was shown that microstructural heterogeneities, such as precipitates and grain boundary segregants, impart an intrinsic susceptibility to the alloy through their capacity for trapping hydrogen and, as a result, generally play a key role in determining the HE resistance observed in practice.

Introduction

The interaction of hydrogen with microstructural heterogeneities in alloys can play a crucial role in determining an alloy's resistance to hydrogen embrittlement (HE). These heterogeneities provide potential trapping sites for hydrogen and so can strongly influence the series of events leading to failure (1). The accumulation of hydrogen at second-phase particles and precipitates, for example, is generally considered to induce particle fracture or weakening of particle-matrix interfaces, thereby promoting microvoid initiation. Large incoherent precipitates tend to be particularly conducive to HE. In general, traps with a large saturability and a high binding energy for hydrogen are conducive to HE, whereas alloys containing a high density of well-distributed irreversible (high binding energy) traps that have a low saturability are considered to be less susceptible (2,3). Thus, the intrinsic susceptibility of an alloy to HE is highly dependent on the type of microstructural defect, with large irreversible traps typically imparting a high susceptibility.

The basic concept of trap theory is that the local concentration of hydrogen trapped at a defect must reach some critical value (C_k) for cracks to be initiated (1,3). It should be recognized, however, that the mechanism by which such an accumulation triggers HE is not addressed. The value of C_k at a potential crack site is determined by the type of trap, its size, concentration (density), and other parameters. A decrease in C_k will render the alloy more susceptible. However, whether embrittlement will actually occur is also affected by the amount of trapped H, which depends on factors such as the entry kinetics, exposure time, and transport mode. In some cases, an alloy may prove resistant during exposure because the amount of H entering the alloy is small enough that the critical concentration at a particular trap is not exceeded. Likewise, when alloys have a similar intrinsic susceptibility in terms of their trapping characteristics, the difference in their actual resistance to HE is likely to be determined by the amount of H absorbed by each alloy.

Over the last few years, the entry and trapping of hydrogen in a wide range of high-strength alloys have been investigated at SRI (4-9). The rates of H entry and rate constants for irreversible trapping were determined using an electrochemical technique referred to as hydrogen ingress analysis by potentiostatic pulsing (HIAPP) (4,10). The research was aimed in part at characterizing the intrinsic susceptibility of the alloys to HE in terms of their irreversible trapping constants. The relative intrinsic susceptibilities then could be compared with results for the actual resistance to HE observed in tests by other workers. A further goal was to determine the trap density where possible and thereby identify the principal irreversible trap in each alloy. In this paper, the irreversible trapping constants and principal irreversible traps for particular groups of alloys are compared, with the objective of rationalizing the role of traps in determining the resistance of these alloys to HE.

Experimental Procedure

In the pulse technique, the alloy of interest is cathodically charged with hydrogen at a constant potential E_c for a time t_c, after which the potential is stepped in the positive direction. H diffuses back to the entry surface and is reoxidized, thereby generating an anodic current transient. Data are obtained over a range of charging times, typically from 5 to 60 s, at different overpotentials ($\eta = E_c - E_{oc}$) relative to the open-circuit potential (E_{oc}), which is measured immediately before each charging time. E_{oc} is also used to monitor the stability of the alloy surface, since any oxides present must not be reduced during charging.

The pulse technique was applied to high-strength steels (4,5), precipitation-hardened and work-hardened nickel-base alloys (4-8), and titanium grade 2 (9). The composition of each alloy is given in Table 5-I. Table 5-II shows the yield strength of the alloys and the thermomechanical treatment used in each case. A number of the alloys contained micrometer-size particles such as carbides or, in the case of 4340 steel, sulfide inclusions.

Test electrodes of each alloy were fabricated from a length (1.3-3.8 cm) of rod press-fitted into a

Table 5-I. Alloy Composition (wt%)

	4340	18Ni	718	925	C-276	625	716	K-500	35N	Ti Gr2
Al	0.031	0.13	0.60	0.30		0.18	0.22	2.92		
B		0.003	0.003							
C	0.42	0.009	0.03	0.02	0.002	0.03	0.011	0.16	0.003	0.021
Co		9.15	0.16		0.83		<0.01		bal	
Cr	0.89	0.06	18.97	22.20	15.27	22.06	20.99		20.19	
Cu	0.19	0.11	0.04	1.93				29.99		
Fe	bal	bal	16.25	28.96	5.84	4.37	5.32	0.64	0.34	0.17
Mn	0.46	0.01	0.10	0.62	0.48	0.17	0.01	0.72	<0.01	
Mo	0.21	4.82	3.04	2.74	16.04	8.70	8.10		9.55	
O	0.001									0.16
Nb+Ta			5.30			3.50	3.47			
Ni	1.74	18.42	54.41	40.95	57.5	60.33	60.5	64.96	35.88	
P	0.009	0.004	0.009		<0.005	0.012	0.004		0.003	
S	0.001	0.001	0.002	0.001	<0.002	0.001	0.001	0.001	0.002	
Si	0.28	0.04	0.11	0.17	<0.02	0.38	0.02	0.15	0.02	
Ti		0.65	0.98	2.11		0.27	1.35	0.46	0.85	bal
W		0.01			3.90					
Other	0.005N	0.05 Ca 0.02 Zr			0.12 V					<0.005H 0.007N

Teflon sheath so that only the planar end surface was exposed to the electrolyte. The surface was polished before each experiment with SiC paper followed by 0.05-μm alumina powder. Details of the electrochemical cell and instrumentation have been given elsewhere (4). The alloys were exposed in a deaerated solution containing 1 mol L^{-1} acetic acid and 1 mol L^{-1} sodium acetate with 15 ppm As_2O_3 added to promote H entry. The potentials were measured with respect to a saturated calomel electrode (SCE). All tests were performed at $22 \pm 2°C$.

Table 5-II. Thermomechanical Treatment of Alloys

Alloy	Heat Treatment[a]	Test Condition	Yield Strength (MPa)
4340	Annealed	HRC[b] 41	1206
		HRC 53	1792
18Ni	Aged (482°C, 4 h)	As received	1954
718	Hot fin., solution treated	As received	1238
925	Hot fin., annealed, aged	As received	758
C-276	Hot rolled	27% cold work	1237
625	Hot fin., annealed	17% cold work	1195
716	Annealed, aged	4% cold work	1186
K-500	Cold drawn, unaged	As received	758
		Aged (600°C, 8 h)	1096
35N	Cold drawn and aged	As received	1854
Ti Gr 2	Annealed (620°C, 1 h)	As received	380

[a] Provided by producer. [b] Rockwell C hardness

Analysis

Although permeation methods have been used extensively, they suffer from several disadvantages, as discussed elsewhere (11). The main theoretical limitation is that most, if not all, diffusion/trapping models for these methods are based on an input boundary condition of constant concentration. Hence, these models are strictly applicable only for charging conditions without any entry limitation.

In the case of HIAPP, a model has been developed to allow for the effect of trapping on diffusion for cases involving either a constant concentration or a constant flux at the input surface (4,10). The constant flux model was found to apply to all alloys studied to date. In this model, the rate of hydrogen ingress is controlled by diffusion but the entry flux of hydrogen is restricted, which results in interface-limited diffusion control. Solution of the diffusion equation for a constant flux condition gives the following expression for the total anodic charge ($C\ m^{-2}$):

$$q'(\infty) = FJt_C\{1 - e^{-R}/(\pi R)^{1/2} - [1 - 1/(2R)]erf(R^{1/2})\} \qquad (5-1)$$

where F is the Faraday constant, J is the entry flux in $mol\ m^{-2}\ s^{-1}$, and $R = k_a t_c$. The charge $q'(\infty)$ is equated to the charge (q_a) passed during the experimental anodic transients. q_a can be associated entirely with absorbed H, since the adsorbed charge is almost invariably negligible.

k_a is an apparent trapping constant measured for irreversible traps in the presence of reversible traps. It is related to the irreversible trapping constant (k) by kD_a/D_L where D_a is the apparent diffusivity and D_L is the lattice diffusivity of H. The magnitude of k depends on the density of particles or defects (N_i) providing irreversible traps, the radius (d) of the trap defects, the diameter (a) of the metal atom, and D_L (12):

$$k = 4\pi d^2 N_i D_L/a \qquad (5-2)$$

The term $d^2 N_i$ represents the trapping capability and underlies the use of k as an index for characterizing an alloy's intrinsic susceptibility to HE.

For the constant flux model to be applicable, it must be possible to determine a trapping constant for which J is independent of charging time. Eq. [5-1] could in fact be fitted to the experimental data for q_a to obtain values of k_a and J that satisfy this requirement at each potential.

The trap density (N_i) can be obtained from k or directly from k_a, according to Eq. [5-3]:

$$N_i = k_a a/(4\pi d^2 D_a) \qquad (5-3)$$

The value of a for an alloy is taken as the mean of the atomic diameters weighted in accordance with the atomic fraction of each element. The trap radius is estimated from the dimensions of heterogeneities that are potential irreversible traps, and trap densities are then calculated for the different values of d. In this way, the dominant irreversible trap can be identified by comparing the values of N_i with the actual concentrations of specific heterogeneities.

The values of k_a and k for the various alloys are given in Table 5-III. Most of the alloys were characterized by a single type of irreversible trap, but alloy C-276 and the 18Ni steel were characterized by both a quasi-irreversible trap and an irreversible trap. In quasi-irreversible trapping, the release constant is not zero but is far too small to achieve local equilibrium between the lattice and trapped H (5).

Among the alloys studied, 4340 steel (HRC 53) has the highest value of k and so can be classified as having the highest intrinsic susceptibility to HE. The 18Ni maraging steel has the next highest k value, followed by various Ni-base alloys, with alloy 625 having the lowest value. Failure tests during cathodic charging have shown that 18Ni (1723 MPa) steel is more resistant to cracking than 4340 steel (13) but that the 18Ni steel in turn will undergo severe HE, whereas alloy 718 exhibits negligible embrittlement (14). Furthermore, ductility losses (14,15) under gas-phase charging suggest that alloy 903 and, by implication, alloy 925 are less sensitive than alloy 718 to HE. Hence, the irreversible trapping constants of the precipitation-hardened alloys, 18Ni, 718, and 925, are consistent with their relative resistances to HE observed in tests.

A similar comparison of the resistances of the work-hardened alloys, C-276 and 625, is complicated by their sensitivity to cold work. However, failure tests have shown that alloy C-276 has a greater tendency to HE than alloy G cold-worked to an equivalent degree (16). Alloys G and 625 are comparable in their levels of Cr, Mo, and — more important — Nb+Ta, so they are likely to be similar in their resistance to HE. Hence, for the degree of cold work involved, alloy C-276 should be less resistant to HE than alloy 625 (6), which matches the order of their trapping constants.

Table 5-III. Trapping Parameters

Alloy	k_a (s^{-1})	D_L/D_a	k (s^{-1})
4340 steel (HRC 53)[a]	0.008 ± 0.001	500	4.0 ± 0.5
18Ni (1954 MPa) steel	0.005 ± 0.002	300 ± 90	1.50 ± 1.05
	0.010 ± 0.005[b]	300 ± 90	3.00 ± 2.40
716 (4% cold work)	0.054 ± 0.004	3.8 ± 0.8	0.20 ± 0.06
718	0.031 ± 0.002	4.0 ± 0.5	0.124 ± 0.024
925	0.006 ± 0.003	5.6 ± 0.6	0.034 ± 0.004
C-276 (27% cold work)	0.025 ± 0.003	3.6 ± 0.8	0.090 ± 0.030
	0.019 ± 0.010[b]	3.6 ± 0.8	0.068 ± 0.051
625 (17% cold work)	0.004 ± 0.002	3.6 ± 0.8	0.014 ± 0.010
K-500 Unaged	0.017 ± 0.003	2.0	0.034 ± 0.006
Aged	0.021 ± 0.003	2.0	0.042 ± 0.006
35N	0.026 ± 0.002	1	0.026 ± 0.002
Ti grade 2 (low H)	0.028 ± 0.002	1	0.028 ± 0.002
(high H)	0.040 ± 0.008	1	0.040 ± 0.008

[a] HRC 41 had the same value of k_a. [b] Quasi-irreversible trapping.

Evaluating the positions of the cold-worked alloys relative to the other alloys is more difficult because of some uncertainty in their values of k. Nevertheless, the trapping constants for alloys

625 and 718 show a significant difference, and the sequence of values is consistent with results from exposure tests that indicated alloy 625 is more resistant to cracking than alloy 718 (17).

If allowance is made for the uncertainty in k, the position of alloy 625 is comparable to that of alloy 35N. Failure tests (18) have indicated that alloy 625 with 17% cold work should be at least as resistant to HE as alloy 35N in the condition of interest (40-50% cold reduced and aged). In fact, the 625 specimen may be more resistant than the 35N alloy, as implied by their k values. Thus, the order of the trapping constants parallels the relative resistance of these alloys to HE.

Ti grade 2 exhibited two values of k (Fig. 5-1), depending on the overpotential and therefore on the level of H in the alloy (9). The similarity in the values of k for low-H Ti grade 2 and alloy 925 fits the relative resistance of these two alloys to HE in that both require long exposure times for their mechanical properties to be degraded (15,19). The higher value of k for Ti grade 2 coincides with its decreased resistance to embrittlement at sufficiently high levels of H (19).

An exception to the above trends was observed with alloy 716, which is an age-hardenable alternative to alloy 625 (17). Alloy 716 had the highest value of k among those for the nickel-base alloys, yet mechanical tests have shown that it is comparable to alloy 625 of similar yield strength in being able to withstand exposure in aggressive environments for periods up to 1000 h (17). A likely explanation is that the H concentration at the dominant traps remains below the critical level required to initiate cracking. In fact, the entry flux of H was low in the acetate buffer and could well have been low enough in the cracking test environments to delay failure (8). Thus, the resistance to cracking observed for alloy 716 was attributed to a low entry flux.

Identification of Traps

The intrinsic susceptibility of an alloy, as noted above, is strongly influenced by the characteristics of its irreversible traps. Identification of the traps on the basis of density and size can be expected to assist in explaining differences in the intrinsic susceptibility of the alloys. Hence, for each alloy, the density of irreversible trap defects calculated from k_a (Eq. [5-3]) was compared with the actual concentration of defects that were assumed to provide the principal traps, as shown in Table 5-IV.
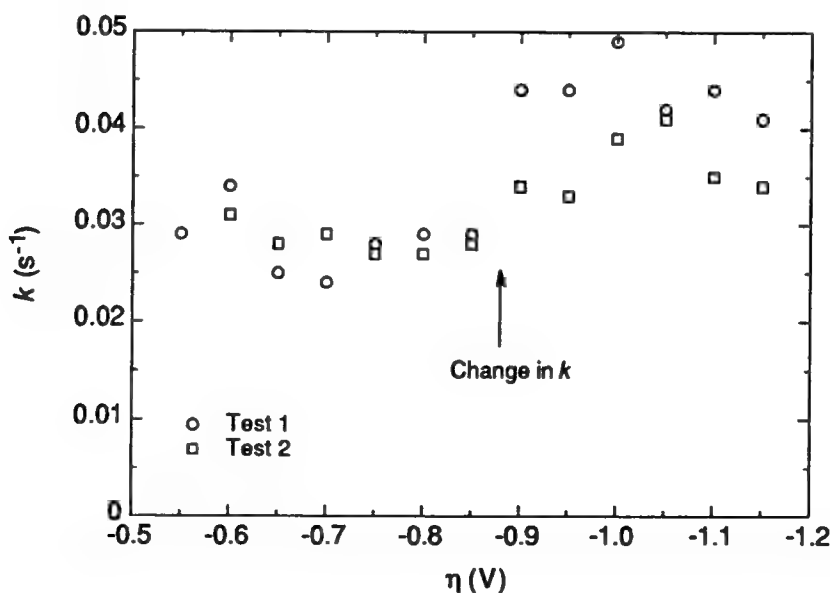

Figure 5-1. Variation in k with overpotential for Ti grade 2 in identical tests.

The Ni-base alloys, 718, 925, 716, and 625, contained carbide or carbonitride particles, which are known to provide irreversible traps in steels (1). The density of irreversible trap defects was therefore calculated on the basis of these particles and was generally found to be in close agreement with the actual concentration of particles, despite some uncertainty in the value of D_a, particularly for alloys 625 and 716. The level of agreement is remarkable, since both the traps and carbides were treated as spherical in calculating the trap density and particle concentration, respectively. However, it indicates clearly that large traps with both a high surface area and a high binding energy can overwhelmingly dominate the irreversible trapping behavior of an alloy.

Table 5-IV. Comparison of Irreversible Trap Densities with Defect Concentrations

Alloy	Defect	Concentration (m^{-3})	N_i (m^{-3})
718	NbTi(CN)	2.2×10^{13}	2.0×10^{13}
925	TiC	4.6×10^{13}	4.1×10^{13}
625	NbTi(C)	7.4×10^{13}	2.5×10^{13}
716	TiC	1.4×10^{15}	1.4×10^{15}
18Ni	TiC/Ti(CN)	1.1×10^{13}	3.4×10^{11}
4340	MnS	2×10^{9}	2×10^{8}
C-276	P (seg)	9×10^{21}	1.9×10^{22}
35N	S, P (seg)	8×10^{21}	8.2×10^{21}
K-500 (Aged)	S (seg)	Not available	2.7×10^{21}

The 18Ni steel contained TiC/Ti(CN) particles, which have been shown to act as strong traps in this type of steel (20). Hence, the irreversible trap density was calculated assuming that these particles acted as the principal traps. The values of N_i and the particle concentration differed by a factor of ~30 but were considered to correlate moderately well, since the difference can be attributed largely to uncertainties in the particle concentration and the value of D_a used for the steel.

The 4340 steel had MnS inclusions, which are prominent irreversible traps in steels (1). The calculated trap density was considered to be in reasonable agreement with the actual concentration of inclusions, since both the inclusions and the traps were assumed to be spherical. Also, N_i did not change significantly with heat treatment, and this lack of change was further evidence that the irreversible traps were associated with the sulfide inclusions.

Segregants

The HE resistance of alloys C-276 and 35N has been correlated with the concentration of S and P segregated at grain boundaries (21,22). Hydrogen segregates to the grain boundaries in Ni (23) and presumably does so in Ni-base alloys, so grain boundary S and P were assumed to provide the irreversible traps predominantly encountered by H in alloys C-276 and 35N. In the case of alloy C-276, it has been suggested that a higher level of grain boundary P may reduce the critical concentration of H required for fracture (21).

In unaged alloy C-276, P is enriched from a bulk concentration of 0.006-0.008 at.% (0.003-0.004 wt.%) to 0.3 at.% at grain boundaries (21). Using the grain boundary concentration, the amount of grain boundary P distributed per unit volume (C_{gb}) of the alloy was estimated in terms of a simple microstructural model based on cubic grains of length b (6). For alloy C-276 in the

condition of interest, $b = 10$ μm and C_{gb} was calculated to be $9 \times 10^{16}/b$, or 9×10^{21} P atoms m^{-3}. The trap density of 1.9×10^{22} m^{-3} calculated on the basis of atomic P was close to the grain boundary concentration, whereas the total P content (taken as 0.004 wt.%) of the alloy corresponded to a much higher concentration, 8.6×10^{24} atoms m^{-3}.

For alloy 35N in the same cold-worked and aged condition used in this study, the level of S and P at grain boundaries has been found to reach 1.6 at.%, compared with a bulk concentration of 0.01 at.% (0.005 wt.%) (22). C_{gb} for segregated S and P in alloy 35N is given by $4.8 \times 10^{17}/b$ atoms m^{-3}. The grains in 59% cold reduced and aged (593°C/4 h) alloy have an average dimension of 60 μm, and using this value gave a C_{gb} of ~8×10^{21} atoms m^{-3}. The trap density calculated in terms of S and P was 8.2×10^{21} atoms m^{-3}, which closely matched the value of C_{gb} but was 3 orders of magnitude less than the total concentration of S and P (0.005 wt.%, or 8.1×10^{24} atoms m^{-3}) in the alloy. The large differences between N_i and the S-P content in alloys C-276 and 35N indicated that the primary irreversible traps were not associated with matrix S and P. In contrast, the close agreement between the values of C_{gb} and N_i, though somewhat fortuitous, was strong evidence that the primary traps were grain boundary S and P.

Ni-Cu base alloys also undergo HE that is assisted by S segregated at grain boundaries (24), so the irreversible trap density for alloy K-500 was calculated on the basis of atomic S. However, the absence of data for S segregation in this alloy meant that the identity of the principal irreversible traps could not be verified by comparing N_i with the grain boundary concentration. On the other hand, it was apparent that the principal traps were not associated with matrix S, since N_i was about 3 orders of magnitude less than the S content (1.6×10^{24} atoms m^{-3}) of the alloy. TiN particles present in alloy K-500 were likewise ruled out as the principal traps because of a large (2 orders of magnitude) difference between the corresponding value of N_i and the particle concentration. In contrast, the results for alloys C-276 and 35N lent some support to the case for considering a grain boundary segregant (in this case, S) as the principal trap in alloy K-500. Further support was provided by recent results for a 77% Cu-15% Ni alloy, which was found to have a higher trap density than that for the 65Ni-30Cu alloy K-500 (7). Even allowing for some difference in the degree of segregation between the two alloys, the higher trap density was consistent with a higher level of grain boundary segregants, based on the higher S-P content (0.015 wt.%) of the 77Cu-15Ni alloy.

Interstitials

The density of traps detected in Ti grade 2 at low H levels was calculated in terms of the minor elements (C, N, O, and Fe). All of the elements except N could be discounted as the principal irreversible trap because of large differences between the values of N_i and the atomic concentrations. Interestingly, among the interstitials, N is particularly effective in reducing the ductility of Ti (25), which coincides with its apparent role as the principal trap. Hence, N may affect the HE resistance of Ti grade 2 through its influence on both brittleness and H trapping.

Hydrides

Evidence of trapping by way of hydride formation was observed in Ti grade 2 and alloy C-276. The increase in k for Ti grade 2 at sufficiently negative potentials ($E_c < -0.93$ V) can be ascribed to an additional irreversible trap that participates concurrently with the N traps. The additional trapping appeared to be associated with accelerated hydride formation that occurs at potentials more negative than -1.0 V (26). The H entry efficiency, which can be calculated from k_a and J, was found to decrease in this region; the decrease was attributed to H entry being partially blocked by a hydride layer (9).

For alloy C-276, the quasi-irreversible trapping was consistent with the formation of an unstable hydride, as found by other workers (27). The quasi-irreversible traps in 18Ni steel, however, were thought to be martensite boundaries, which are moderately strong traps in this type of steel

(20). A trap density of 9×10^{17} m^{-3} was calculated in terms of the martensite boundaries, which, like grain boundaries (28), were assumed to have an influence diameter of 3 nm.

Discussion

The alloys in this work were typically characterized by a single irreversible trap, but in some alloys the principal trap was supplemented by another irreversible trap or a quasi-irreversible trap. Values of k associated with the principal irreversible traps are presented in Fig. 5-2 for all the alloys except 716. The steels, particularly 4340, exhibited high values of k that were indicative of a high intrinsic susceptibility to HE, whereas the nickel-base alloys were characterized by lower values of k and therefore were intrinsically less susceptible. Differences in the susceptibility of the nickel-base alloys were smaller than those for the steels but were clearly discernible, as shown in Table III.

Most of the alloys appear to show a correlation between the intrinsic susceptibility, as represented by k, and the actual resistance to HE observed in mechanical tests. This correlation suggests that, for these alloys, the observed resistance to HE was determined primarily by the alloy's intrinsic susceptibility — that is, by the irreversible trapping characteristics. Thus, while factors such as the entry flux and stress level may be important, they seem to have had only a secondary effect on the HE resistance in most cases. Exceptions to this correlation can occur in cases such as alloy 716, where the entry flux is low enough that the alloy is relatively resistant to cracking, even though it might have a high intrinsic susceptibility.
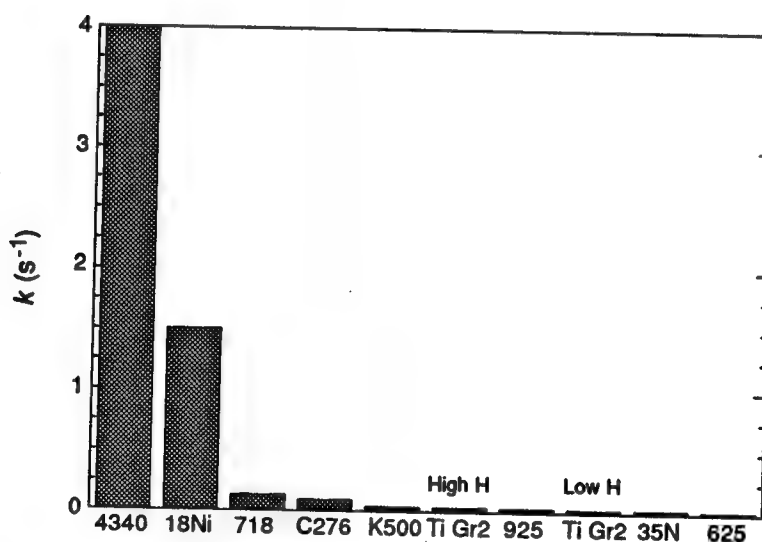

Figure 5-2. Variation in k for the different alloys.

The use of k to provide an index of HE susceptibility can be justified on the basis of Eq. [5-2], but there remains the question of why such a relatively simple parameter has the apparent ability in most cases to indicate the relative resistance observed to HE. Some insight may be gained by considering k, which encompasses the trapping capability ($d^2 N_i$) as well as the alloy-specific characteristics of metal atom size and lattice diffusivity. For simplicity, the defects providing the principal traps are assumed to be similar in size (d), with the critical concentration (C_k) at each of these defects having roughly the same value. The trap defect size has a strong influence on C_k and is incorporated as an area term in the trapping capability together with the density of potential crack

sites possessing this C_k, while the diffusivity reflects the ease of H transport to different sites, including traps. Since the likelihood of crack initiation is highly dependent on both C_k and H accumulation as well as the availability of sufficiently large defects, it is perhaps not surprising that k is effective as an index of susceptibility in being able to indicate the actual resistance of most of the alloys to HE. Underlying this rationale is the implication that, despite differences in the H entry flux between the alloys, the flux was generally not low enough to become the controlling factor.

The nature of the irreversible trap defects appears to play a significant but not exclusive role in determining the intrinsic susceptibility of an alloy. Alloys such as 718 and 4340 steel, in which the principal traps are large second-phase particles, typically exhibited a high intrinsic susceptibility ($k > 0.1$ s^{-1}), whereas other alloys do not show a relationship between the susceptibility and the type of irreversible trap, whether it be particles, segregants, or interstitials. However, the microstructural features that provided the principal traps in the different alloys had a wide range of sizes and concentrations, and for alloys with comparable H diffusivities, the resulting diversity in trapping capabilities produces considerable differences in the intrinsic susceptibilities to HE. In cases where the values of D_L are similar, k is predicted to increase linearly with $N_i d^2$ (Eq. [5-2]). Fig. 5-3 shows the dependence of k on $C_p (d_p/2)^2$ for the four alloys (625, 716, 925, and 718) containing carbides or carbonitrides, where C_p and d_p are the concentration and characteristic dimension, respectively, of the particles. Although the amount of data is limited and the value of D_a for alloy 625 is uncertain, a linear relationship seems to exist, which underscores the fact that the carbide/carbonitride particles appear to be primarily responsible for irreversible trapping in these alloys.

Summary

For a wide range of alloys, a correlation exists between the intrinsic susceptibility, as defined by the irreversible trapping constant, and the observed resistance to HE. Thus, the HE resistance appears to be determined primarily by the alloy's intrinsic susceptibility. This relationship implies that the H entry flux generally has only a secondary effect on the HE resistance for most of the alloys, which suggests that the flux is usually not low enough to become the controlling factor.
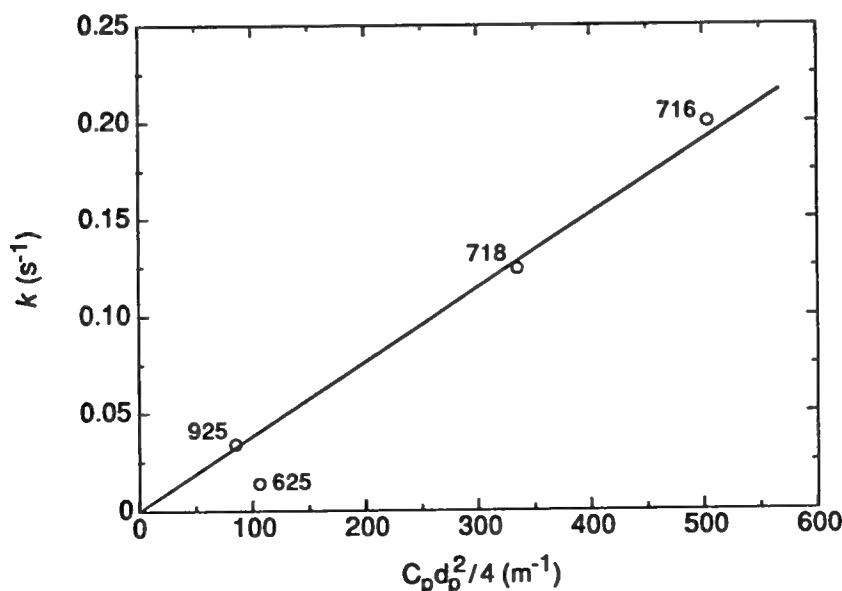
Figure 5-3. Dependence of k on $C_p (d_p/2)^2$ for Ni-base alloys containing particles.

However, in one case (alloy 716), the resistance to HE can be attributed to a low entry flux. The irreversible trapping constant, by virtue of the observed correlation, appears able to indicate the relative resistance to HE for all the alloys except 716. This ability of k seems to be attributable to its dependence on both the trapping capability and the diffusivity. The combination of these two characteristics is crucial for crack initiation and therefore provides a rationale for the correlation observed between k and the resistance to HE. Various microstructural features can be identified as the principal irreversible traps, either singly or in the presence of multiple principal traps. Although k is affected by the diffusivity, the variation in intrinsic susceptibility of the different Ni-containing alloys generally seemed to result from differences in the trapping capability caused by the diversity of sizes and concentrations of the microstructural defects.

Acknowledgment

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Addendum

The concepts explored in the review above attempt to bring together the various aspects of hydrogen embrittlement ranging from hydrogen entry through trapping to cracking. These concepts could not be adequately discussed in the review and are therefore considered in more detail below.

Intrinsic Susceptibility to HE

The intrinsic susceptibility to HE is affected by a range of factors, but some of them would be expected to exert a greater influence than others and so be primarily responsible for determining the susceptibility. The irreversible trapping constant (k) that was used as an index of the intrinsic susceptibility incorporates several key parameters: trap size, trap density, lattice diffusivity, and metal atom size. The local mechanical conditions are addressed to some extent through the trap size in the case of particles because of the strong influence that trap size has on the critical concentration (C_k). C_k is the concentration of H required to cause enough of an increase in the induced and applied stresses and/or the hydrogen pressure to overcome the cohesive strength, which itself may be decreased (1). Since larger particles lead to higher local stress concentrations, the trap size affects C_k (in part) by affecting the difference between the local stresses and cohesive strength. Hence, k, in allowing for trap size, implicitly contains some allowance for the effect of the local stress/cohesive strength conditions on C_k.

The correlation between k and the observed resistance to HE suggests that k contains enough key parameters to be effective as an index of susceptibility for the alloys studied at their respective yield strengths. The correlation for the high-strength steels is supported by recent trapping data for the aged martensitic steel, AerMet 100 (yield strength = 1834 MPa) (2). The order of the irreversible trapping constants for 4340 steel, 18Ni steel, and AerMet 100 ($k = 0.41$ s^{-1}) is consistent with their threshold stress intensities for stress corrosion cracking. Thus, it seems increasingly unlikely that the correlation for the high-strength steels is fortuitous. However, it is possible that factors other than those above could assume a greater role at low yield strengths, such that k becomes inadequate as an index of susceptibility.

At high yield strengths, k must decrease with decreasing yield strength of these steels, if it is to be consistent with the reported increase in K_{ISCC} (3,4). The lattice diffusivity (D_L) and therefore k could be affected by the microstructural changes that occur as the tempering temperature is increased (yield strength decreased). However, it can be difficult to find appropriate values for D_L because the measured diffusivities are usually affected by trapping. For the 4340 and 18Ni steels, D_L was taken to be the diffusivity for α-Fe and Fe-18Ni, respectively, but it would have been more appropriate to use the diffusivity, if it were available, for the corresponding tempered martensitic lattice. It has been shown for a high-strength martensitic steel containing 0.4C-0.6Mn-0.3Ni (compared with 0.42C-0.46Mn-1.74Ni in the 4340 steel) that the diffusivity decreases as the tempering temperature is increased above the point where ε-carbide precipitation is essentially complete and quenched-in lattice defects have largely been relieved (5). Thus, although part of this decrease probably resulted from reversible trapping, it seems that a decrease in D_L is quite plausible in the case of 4340 steel.

The value of k for 4340 steel could also change because of a change in the type of principal irreversible trap and therefore in $N_i d^2$. Sulfide inclusions are important irreversible traps in 4340

steel, as shown by thermal desorption results (6) and by differences in H absorption and outgassing between different grades of 4340 steel (7). However, incoherent Fe_3C and high angle grain boundaries can also act as irreversible traps, though their presence in 4340 steel depends on the tempering conditions (8). It has been found that MnS inclusions act as traps in a low alloy steel (0.34C-1Cr) tempered at 300°C, and precipitates come into play in specimens tempered at 600°C (9). Hence, it is possible that sulfide inclusions provide the predominant irreversible traps in 4340 steel at very high yield strengths (low tempering temperatures) where there is negligible Fe_3C and another defect becomes the principal trap as the yield strength is decreased.

The cracking behavior of 4340 steel is strongly influenced by the relative importance of the different irreversible traps (8). Prominent particle-type traps such as large (even round) inclusions have a high probability of cutting or lying along grain boundaries, and cracks initiated at the inclusions are then likely to follow the relatively susceptible grain boundary (10). The importance of each trap depends on its density and size, so cracking can be affected by the grade of 4340 steel and its yield strength (heat treatment) as well as by the level of elements such as Mn (11)—Mn, for example, is detrimental (12) when segregated to grain boundaries in high strength steels. It is therefore important that the interpretation of cracking behavior in terms of trapping be made on the basis of comparable specimens for the respective tests.

The possibility also exists that some type of defect other than sulfide inclusions provides the principal irreversible trap in 4340 steel, even at high yield strengths. The trap density calculated on the basis of sulfide inclusions differed from the actual concentration of inclusions by a factor of 10, which was regarded as being reasonably close. (It was also reported that N_i did not change significantly with heat treatment, but this conclusion was based on the rough approximation that D_a did not vary significantly with heat treatment.) However, this difference may imply that the sulfide inclusions were not the principal traps. If incoherent Fe_3C or high angle grain boundaries were the principal traps, $N_i d^2$ and therefore k for 4340 steel would be expected to change with heat treatment.

In maraging steels, the resistance to H-assisted cracking (generally intergranular) is thought to be lowered by Ti(CN) particles (4). Autoradiography has shown that hydrogen trapping occurs at the carbonitride interfaces in maraging steels, and this trapping is reported to be strong enough to explain crack initiation; the interface between the carbonitride particle and its matrix appears to be weakened by trapped hydrogen (13). The trap density and concentration of TiC/Ti(CN) particles in the 18Ni steel used in the present work differed by a factor of ~30 but were considered to be moderately close, for reasons given in the paper. As with 4340 steel, this difference may in fact indicate that these particles were not the principal traps. Still, the carbides/carbonitrides were >1 µm in size, which puts them in the category of detrimental—rather than beneficial—traps, as designated by Bernstein and Pressouyre (14). In the case of the Ni-base alloys, carbides and carbonitrides were generally identified as the principal traps, and various studies have shown that fracture is typically initiated by void formation at matrix carbides (15).

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Verification of Diffusion/Trapping Model

Both a constant concentration and a constant flux have been assumed as the input boundary condition in models for hydrogen diffusion in metals; however, models that allow for trapping in the conventional permeation methods deal only with the constant concentration case. Limitations in the use of a constant concentration boundary condition have been discussed elsewhere (1). In our work, the constant flux model was found to apply to all the alloys studied under the charging conditions imposed by the pulse technique. As noted in the paper, it was possible to determine a trapping constant for which the entry flux was independent of charging time at each potential. This condition had to be satisfied for the model to be applicable. Also, the trapping constant was independent of charging potential (except when a change in trapping behavior occurred), as is required for the model to be valid, since the trapping characteristics at low occupancy should be unaffected by electrochemical conditions at the metal surface. Any attempts to apply the constant concentration form of the diffusion/trapping model to these alloys have been unsuccessful.

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Effect of Different Irreversible Traps

It must be emphasized that the observed correlation between the intrinsic susceptibility, as defined by k, and the observed resistance to HE applies to the specific alloys studied in their particular thermomechanical conditions. This correlation may not extend to these alloys at lower yield strengths or to other alloys. As noted in the paper, exceptions to the correlation can occur when the entry flux is so low, as with alloy 716, that it becomes the primary factor in determining the resistance to HE.

Defect size can also be an important factor. Your work (1) has shown that homogeneously distributed, small particles (<<1 µm for α-Fe) that are irreversible traps can be beneficial. Thus, the addition of small particles imparting high values of C_k to a metal that is otherwise free of irreversible traps would not be expected to reduce the resistance to HE. On the other hand, these particles are supposedly small enough that the concentration of trapped H (C_H) cannot reach C_k, so their presence will not increase the intrinsic susceptibility. Accordingly, k should not be used as an index of susceptibility in this case; the relationship between k and $N_i d^2$ (Eq. [5-2] in the review) implicitly applies to particles that are large enough for C_H to be able to reach C_k. If detrimental traps are present in an alloy, the addition of small particles will increase the HE resistance by delaying the accumulation of H at the detrimental traps. In this sense, small particles can have the same effect as a decrease in the entry flux.

In practice, *most* irreversible traps are characterized by large specific saturabilities, as noted by Gibala and DeMiglio (2). The majority of the engineering alloys in our work contained carbides, carbonitrides, or sulfides that were in the form of large particles (>1 µm and typically several micrometers) and, as might be expected, it was these particles that provided the principal irreversible traps. Such particles are known to be conducive to HE, particularly if they are distributed heterogeneously (1). Thus, the addition of large traps, unlike small traps, increases the intrinsic susceptibility (higher k) and is expected to result in a corresponding decrease in the actual resistance to HE, which fits with the observed correlation.

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